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An Experimental and Numerical Study of the Oxidation/Combustion
Reaction Kinetics in High Pressure Air Injection Process

by

Yalda Barzin

A THESIS

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UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "An Experimental and Numerical Study of the Oxidation/Combustion Reaction Kinetics in High Pressure Air Injection Process" submitted by Yalda Barzin in partial fulfilment of the requirements of the degree of Doctor of Philosophy.

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Abstract

High Pressure Air Injection (HPAI) as an enhanced oil recovery method has received notable attention during the last decade after its first successful application in Buffalo Red River Unit project. Since then, several other field projects have been initiated and investigations have been carried out to develop the understandings of the controlling mechanisms. Reaction kinetics of the oxidation/combustion reactions are the most crucial mechanism. They control the overall performance and success of air injection processes; however, they are not fully explored for light oils (or even heavy oils) yet. Lack of a reliable kinetics model for incorporation into field numerical simulations has been a limiting factor to the prospective vast applications of HPAI as an enhanced recovery method.

This dissertation was assigned to provide a proper kinetics model for light oils oxidation/combustion reactions under HPAI, through laboratory studies and numerical simulation. For the purpose of this research, a high pressure ramped temperature oxidation reactor (HPRTO) was designed. 15 air injection and nitrogen injection experiments were conducted on the mixture of light oil, water, and core. Nitrogen injection tests were performed to study the distillation behavior and characterize the evaporation drive mechanism and its potential associations with the reaction kinetics; while, air injection tests aimed at understanding the scheme and kinetics of the chemical reactions occurring during HPAI. Also the effect of the operating parameters on the overall outcome of the process was studied with a focus on oil composition, injection gas flux, and initial water saturation.

A comprehensive equation of state phase behavior model using data generated through several PVT tests was developed. A methodology was proposed to employ the phase behavior model and generate compositional equilibrium K-values under conditions of the HPRTO tests. Based on the data, observations, and understandings achieved during the

course of the experimental study, a reaction kinetics model was set up. This primary kinetics model was later incorporated into a thermal numerical simulation model to replicate the behavior of the conducted air injection tests. After fine tuning of some kinetic parameters against the experimental data, the final proposed model was verified by its successful application to two other different cases.

The significant finding of this research, which also composed the core of the proposed kinetics model, was the recognition and characterization of the potential vapor phase combustion reactions during the HPAI process.

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To my parents
Shahin and Hossein

and my husband
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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
A	Cross Sectional Area, m ²
A	Pre Exponential Factor, 1/kPa.s
API	American Petroleum Institute
API°	Specific Gravity in API Units (= 141.5/SG – 131.5)
ARC	Accelerating Rate Calorimeter
C	Molar Concentration
CCE	Constant Composition Expansion
Cum.	Cumulative
DSC	Differential Scanning Calorimeter
DTA	Differential Thermal Analyzer
E	Activation Energy, J/gmol
EOR	Enhanced Oil Recovery
EOS	Equation of State
FVF	Formation Volume Factor
GC	Gas Chromatograph
GOR	Gas Oil Ratio
H/C	Atomic Hydrogen to Carbon Ratio
HO	Heavy Oil
HPAI	High Pressure Air Injection
HPRTO	High Pressure Ramped Temperature Oxidation
HTO	High Temperature Oxidation
ISC	In Situ Combustion
K	Permeability, D
L	Length, m
L	Liquid
LO	Light Oil

LTO	Low Temperature Oxidation
m	Reaction Order With Respect To Oxygen
MO	Medium Oil
MTO	Medium Temperature Oxidation
n	Reaction Order With Respect To Fuel
P	Pressure, kPa _g
PDSC	Pressurized Differential Scanning Calorimeter
PVT	Pressure-Volume-Temperature
q	Injection Gas Flux
R	Reaction Rate
R	Universal Gas Constant
ROV	Relative Oil Volume
RTO	Ramped Temperature Oxidation
S	Solid
S	Saturation
sm ³	Standard Cubic Meters (15°C and 101.325 kPa)
SARA	Saturates-Aromatics-Resins-Asphaltenes
SCN	Single Carbon Number
SG	Specific Gravity
T	Temperature, °C
TGA	Thermo Gravimetric Analyzer
V	Vapor
VCT	Virtual Combustion Tube
X	Composition
Z	Compressibility Factor

Subscripts

<i>c</i>	Combustion
<i>c</i>	Critical Property

f	Fuel
g	Gas
i	Component i
l	Liquid
o	Oil
r	Relative
w	Water
x	Number of Carbon Atoms
y	Number of Hydrogen Atoms

Greek Symbols

α	Conversion Factor
γ	Activity Coefficient
ν	Proportionality Factor
ρ	Density, kg/m ³
φ	Fugacity Coefficient
Φ	Porosity
ω	Acentric Factor

Chapter One: Introduction

1.1 Background

Almost 70% of the world's oil and gas production comes from the mature fields. Currently, operators are facing a dual challenge: the urge to improve the profits from their resources while the rate of discovery of new major fields has been declining over the last few decades. The oil and gas market analysts believe that most of the world's giant field have been already explored. With fewer field discoveries and more mature fields, the importance of exploiting the producing fields to an ultimate oil recovery comes to light. Mature fields still contain around 65% of their original oil on average. Given the high amounts of reserves left in these fields, according to Halliburton (2008), "every percentage point increase in recovery can generate a two-year global supply of hydrocarbons."

During its production life, a conventional oil reservoir goes through a few phases. The first phase is depleting the reservoir off the portion of its oil that can be recovered without any intervention. High rates of production followed by a relatively quick decline marks this period. The field is considered as mature at this point and all of its "easy hydrocarbons" are produced. Next phase is the industry-standard secondary recovery which includes water injection and artificial lifts to manage the reservoir pressure and generate additional oil flow. This phase is augmented by drilling, re-completion and optimization of water flood. Enhanced oil recovery is the last phase and it employs techniques such as gas/air, steam, and chemical injection. It also deals with development of new facilities to increase the oil recovery. Figure 1-1 depicts the recovery factor from a mature field alongside the incremental recovery each of the recovery stages have to offer.

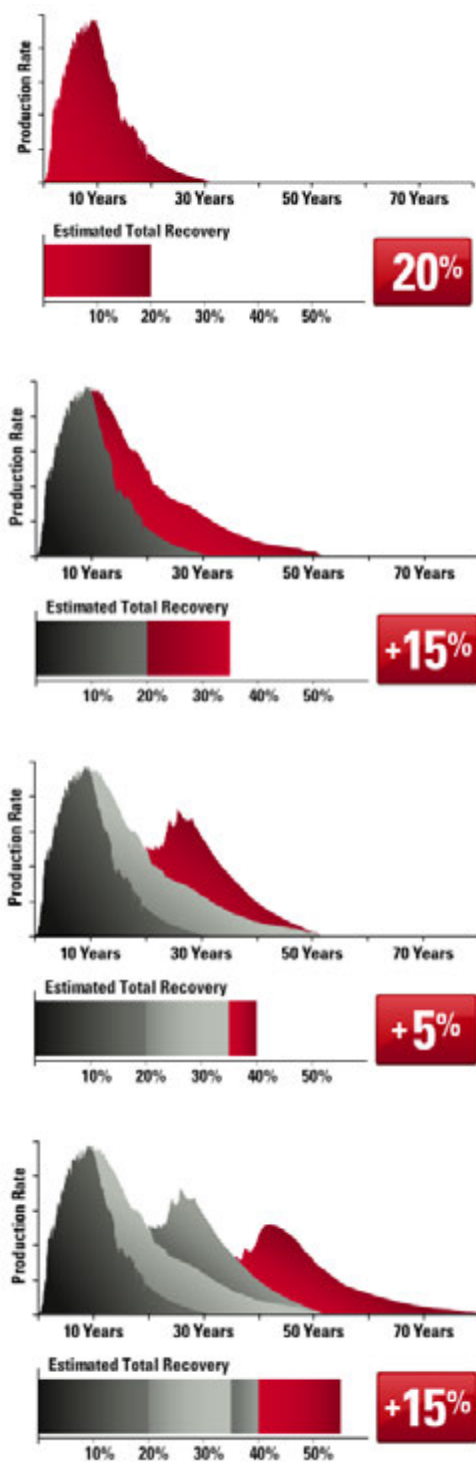


Figure 1-1 Primary, Secondary, Improved (IOR) and Enhanced (EOR) Oil Recovery
(Courtesy of Halliburton, 2008)

Among the EOR methods applied in conventional oil reservoirs, High Pressure Air Injection (HPAI) has been a subject of increasing worldwide attention during the last decade. HPAI is a thermal air injection method suitable for deep, high temperature, light oil reservoirs. It is promising in particular for the tight, remote or offshore reservoirs. Although air injection in heavy oil reservoirs, known as *In Situ* Combustion (ISC), has been around since 1950's and is currently active in Canada, Romania, India, and U.S., HPAI is a relatively young method. The success and expansion of the HPAI projects in Montana and North and South Dakota has contributed to a steady increase of the HPAI projects in the area since year 2000. West and South Buffalo, and Medicine Pole Hill in North and South Dakota are good examples of successful application of HPAI to light oil formations.

In addition to the achievements from U.S. projects in Williston Basin, results of the HPAI pilots in Handil Field, Indonesia and Hu 12 Block, Zhong Yuan field in China have been reported as encouraging by Duiveman *et al.* (2005) and Hongmin *et al.* (2008) respectively. Increased interest in HPAI is also significant from studies reported by Hughes and Sarma (2006), Sarma and Das (2009), Teramoto *et al.* (2005), Onishi *et al.* (2007), and Rodriguez and Christopher (2004) on feasibility of HPAI in Australia, Asia, and Mexico. Manrique *et al.* (2010) reviewed the current status and future opportunities of EOR methods and suggested that based on the recent trends, HPAI will continue to grow in the next decade.

Although HPAI has proven to be economically attractive, a core solid understanding of the mechanisms involved in the method is yet a challenge. In HPAI, compressed air is injected to a deep light oil reservoir. A small fraction of oil reacts with oxygen from the air and generates *in situ* heat, water, and flue gas. HPAI benefits from the thermal drive mechanism imposed by the combustion reactions, swelling of the oil and viscous drive

by flue gas, and distillation/steam distillation at elevated temperatures. Therefore, it is a complex method in the sense that it is associated with simultaneous heat transfer, mass transfer, chemical reactions, multi phase flow, and phase changes. While heat transfer and fluid dynamics of air injection processes are relatively well understood, the kinetics of oxidation/combustion reactions coupled with mass transfer and compositional changes are still subject to challenges. Kinetics of heavy oil oxidation/combustion reactions, owing to more than 60 years of ISC history, are partially understood and reported in the literature; however, the oxidation/combustion behavior of light oils remains uncertain.

In an HPAI process, distillation of lighter components causes transfer of hydrocarbons through the vapor phase towards the cooler parts of the reservoir. Also it provides the possibility for the hydrocarbons in the vapor phase to engage in oxidation reactions, whenever conditions are favorable. It is commonly accepted that the chemical reactions dictate the overall success of an air injection process. However a comprehensive study on chemical reactions occurring during HPAI and their kinetics is lacking in the petroleum literature. Although HPAI and ISC methods are similar in many ways, kinetics of chemical reactions and phase behavior of the fluid model need further studies.

Due to changes in pressure, temperature, and composition with time and space during an HPAI process, phase behavior is very important. Light oils go through a high degree of vaporization/condensation and in the presence of active chemical reactions a high degree of compositional change is expected. To date, no commercially available thermal numerical simulation software that is furnished with a fully compositional phase behavior model is formulated. When employing the existing ISC numerical models to simulate an HPAI process, care must be undertaken to adequately model phase behavior, and reaction kinetics.

This study was assigned to address the reaction kinetics and distillation aspects of HPAI. Physical and Numerical simulations were used to build a new set of kinetic models to incorporate into HPAI numerical simulation software.

1.2 Statement of the problem

Complexity of air injection process due to co-occurrence of several mechanisms during its application has been continuously challenging the researchers for the past 60 years. Numerous researchers have attempted to characterize the effects of heat transfer, mass transfer, chemical reactions, and phase behavior on the overall performance and recovery of an air injection project.

It has been acknowledged that the chemical reactions and their kinetics play a major role on the success of both light and heavy oil air injection processes. Light oil reactions have been characterized mostly using conventional heavy oil kinetic models. However, sensitivity of the reaction kinetics to phase behavior and compositional changes in light oils call for a comprehensive study of kinetics of light oil oxidation.

The key objective of this study has been understanding and incorporation of vapor phase combustion reactions into a kinetics model which integrates the hydrocarbon compositional changes and energy generation characteristics of the so called LTO reactions. There is essentially no information on the liquid and vapor phase oxygen addition reactions for light hydrocarbons within the open literature and there is no recognition of the importance of flammability limits on the bond scission or combustion reactions which occur in the vapor phase.

Phase equilibrium between the liquid and vapor phase hydrocarbon and water components have a significant impact on the flammability range for vapor phase combustion at a given temperature. The composition of the combustible fractions in the

vapor phase can be estimated based on the composition of the original oil; however, the generation of vapor phase fractions due to low temperature cracking of LTO products in the liquid phases will have a significant impact on the flammable range for the vapor phase combustion reactions. In situ combustion literature has generally not incorporated the “flammable range concept” into combustion models as it is not possible to directly control this parameter as is done in a conventional combustor or engine. This does not mean that the “flammable range within the vapor phase is not important” as it has a very significant effect on the rate of oxygen consumption by the bond scission or combustion reactions.

Given the importance of vapor phase behavior on the amount and distribution of hydrocarbons available for reaction with oxygen, a comprehensive phase behavior study is required to understand the compositional changes of the phases and the parameters affecting the phase behavior of light oils during HPAI oil recovery processes.

This research presents a laboratory methodology based on High Pressure RTO (HPRTO) experiments, programmed to provide comprehensive data in order to improve understandings of light oil combustion and develop a proper kinetic model.

1.3 Objective

To build a set of reaction kinetic models for light oil air injection. The specific objectives of this research include:

1. To understand the role of vapor phase combustion in light oil combustion and the impact of vapor phase flammability range
2. To evaluate the contribution of distillation, flue gas drive, and thermal effects (associated with the oxidation/ combustion reactions) to the overall oil recovery

3. To characterize the effect of distillation on the observed oxidation/ combustion kinetics
4. To characterize the effect of interstitial water on the overall oxidation behavior of light oil (by heat transfer and phase behavior)
5. To investigate the spontaneous ignition phenomenon in light oils

1.4 Outline of the Dissertation

Chapter two provides a review on the previous experimental and numerical studies conducted to characterize various aspects of HPAI, with an emphasis on reaction kinetics and phase behavior models.

Chapter three describes the laboratory methodology designed for the purpose of this study including the high pressure RTO experimental apparatus and procedure; pre-test and post-test analyses; test design strategies and operational conditions.

Chapter four describes all 15 nitrogen injection and air injection experiments performed on the HPRTO reactor.

Chapter five presents a discussion of the findings from the experimental study. The concepts of “vapor phase combustion” and “flammability” are introduced and expanded. Based on the information from experiments, conditions under which vapor phase reactions may be active are highlighted.

Chapter six explains the development of the compositional phase behavior model and compares the K-value results with conventional non-compositional K-values.

Chapter seven introduces the numerical simulation of the HPRTO tests. It presents how the findings from the experimental and phase behavior parts of this study have been

incorporated to build the proposed reaction kinetics model. The numerical simulation model including the reaction kinetics model is verified against various tests and operational conditions and results are reported.

Chapter eight summarizes the conclusion and suggestions for consideration in the future HPAI studies.

Chapter Two: Literature Review

High Pressure Air Injection (HPAI) is an enhanced recovery method for light oils which benefits from thermal effects, distillation/steam distillation, and flue gas drive. The perspective for HPAI is to produce in situ heat and flue gas through oxidation of a small portion of the in place oil with the oxygen from the injected air at elevated temperatures. Several complex parallel mechanisms are involved in HPAI, namely chemical reactions, heat transfer, mass transfer, multi phase flow, and phase.

HPAI in many aspects is similar to In *Situ* Combustion (ISC), which is the air injection recovery method applied to heavy oil reservoirs. Owing to its long history, some ISC basic knowledge and experiences have been directly applied to the HPAI studies. While chemical reactions and their kinetics are the most dominating mechanisms in both ISC and HPAI, the type and nature of these reactions in these two processes may be different. This chapter is primarily a review of the fundamental experimental studies which were mostly aimed at understanding the oxidation/combustion behavior of crude oil under ISC. The basic types of kinetic models which have been developed supported by the experimental data will be covered next. Finally, several numerical simulation models will be reviewed with an emphasis on light oils and their sensitivity to thermodynamic phase behavior and the equilibrium K-values. The theme of this last section will be to investigate whether and how different researchers have considered gas phase oxidation/combustion reactions in light oil air injection.

2.1 Kinetic studies of oxidation/combustion reactions

2.1.1 Experimental studies

The experimental techniques designed for kinetic studies of oxidation/combustion reactions generally fall into two categories of quantitative and qualitative (“fingerprinting”) studies. The qualitative investigations assume a simplified reaction model applied to a sample of oil under conditions that do not represent the actual reservoir conditions, mainly in terms of thermodynamic and multi-phase flow. Therefore, this class of experiments are observation aids which contribute to explore a particular oil's oxidation/combustion behavior, including its exothermicity and ability to develop and sustain a combustion reaction at certain temperature levels. Generally, the reservoir conditions are better replicated in quantitative studies, where calculated kinetic parameters are more accurate. Experimental set-ups used for “finger printing” studies are in essence thermal analysis tools, namely TGA (Thermo-gravimetric Analyzer), DTA (Differential Thermal Analyzer), DSC and PDSC (Pressurized/Differential Scanning Calorimeter) and ARC (Accelerating Rate Calorimeter). These techniques are widely used for kinetic studies of oxidation/combustion reactions and screening of the oil for *in situ* combustion application.

In these thermal techniques, a small sample of the oil is heated at a defined rate (except in an isothermal test) under air or nitrogen flow and the changes in sample's weight, temperature, or energy are recorded and plotted against temperature. The DTA, TGA curves are known as thermograms and are unique characteristics of each crude oil. The weight loss or temperature/energy change of the samples can be interpreted as indicators of different dominating mechanisms over certain temperature ranges, such as distillation, cracking, oxidation or combustion reactions. However, TGA, DTA, and DSC are limited to low and medium pressure operations. ARC was developed in the early

1980s to study the exothermic reactions at elevated pressures (up to 41 MPa). Although these thermal techniques are acceptable qualitative screening tools, they are limited to a semi-batch system with a stationary oil sample. Furthermore, the kinetic models based on these techniques often consider a single reaction model which is not adequate for a rigorous representation of reservoir reaction conditions.

Apart from this group of tests, Ramped Temperature Oxidation (RTO) experiments are designed to replicate the flow conditions in a plug flow reactor cell containing a sample of oil, water and sand. These tests, also known as effluent gas analysis, provide quantitative data for calculations of kinetic parameters. However, for in situ combustion design parameters such as the fuel availability, air requirements, etc., combustion tube tests are necessary to provide the comprehensive set of experimental data and observations. The following section will provide a review on some fundamental experimental studies which employed these techniques to develop understandings of crude oils' oxidation/combustion behavior, different classes of reactions occurring in the air injection process, and the kinetic parameters associated with these reactions.

In the classical in situ combustion literature, fuel deposition is normally attributed to the mechanism through which the portion of the oil that will be later consumed by the combustion reactions is left on the surface of the sand matrix after a pyrolysis reaction. The fuel is widely assumed to be a solid-like residue (typically referred to as coke) and/or a heavy portion of the liquid oil (asphaltenes). The general form of the pyrolysis reactions will be described through Equation 2.15 in the following subsection (2.1.2). In a preliminary study of fuel deposition in air injection processes, Bae (1977) developed DTA and TG instruments which could operate at pressure and temperatures as high as 537 °C and 6.8 MPa respectively. The produced thermograms for the 15 different examined oils, of a variety of gravities (6 to 38 °API), showed three distinctive patterns,

which didn't necessarily correlate with the gravities of the crude oils. Presence of air at low temperatures drastically changed the quality and quantity of fuel deposition. For most of the studied samples at 345 kPa_a and up to 260 °C almost a 60% weight loss was observed in the presence of nitrogen or air. Distillation was recognized as a dominant mechanism for fuel deposition. A lesser degree of distillation at higher pressures would result in more available residual fuel. Also the significance of heat generated by oxidation addition type reactions was highlighted by the thermograms obtained in this study.

Vossoughi and El-Shoubary (1989) employed the TGA technique, subjecting a 19.3 °API oil to oxygen flow at constant heating rates. They investigated the effect of oil saturation, oxygen partial pressure and specific surface area on crude oil coke combustion. Crude oil content was varied between 10 and 58 wt% and the oxygen partial pressure was between 5 and 50 kPa. The lower oxygen partial pressure limit was associated with no exothermic reaction zone, where the upper limit led to a sudden flash of oil into flame. Three major transition zones were indicated by the thermograms: distillation, low temperature oxidation (LTO), and high temperature oxidation (HTO). Detailed descriptions of these classes of reactions are provided in section 2.1.2. A power-law model was introduced to correlate the rate of disappearance of the reactant (coke combustion) to the oxygen partial pressure and sand surface area. The model was validated by testing a variety of crude oils from US, and Canada.

Yannimaras and Tiffin (1995) modified the ARC (Accelerating Rate Calorimeter) technique for applicability in kinetic studies of crude oils at reservoir conditions. Design of the ARC enables operation at high pressure conditions (up to 41 MPa) which is a desired capability compared to other thermal "screening" methods. The ARC's differentiating characteristic or its "heat-wait-search-adiabatically-follow-exotherm" mode

of operation reveals the oil's thermal potential for spontaneous ignition and continuity in combustion. In their paper, Yannimaras and Tiffin discussed the ARC test results for four different crude oils with medium and light gravities. They compared the results of ARC tests with the combustion tube test data available for these oils to draw on how ARC test results can be tied to combustion tube data to predict the performance of the air injection process, mostly based on ignition and continuity of the combustion reactions.

In the category of quantitative kinetic studies, the RTO (Ramped Temperature Oxidation) test is the most representative as it allows the study of the global oxidation behavior and reaction kinetics under controlled gas flow at reservoir pressure conditions. Different designs for RTO apparatus are described in the literature. Burger and Sahuquet (1972) characterized the oxidation behavior of a 27 °API oil at 557 kPa_a using the RTO set-up at the Institut Francais du Petrole. They also investigated the effect of additives (copper derivative and nickel oxide) on the combustion behavior of the oil and on coke formation. During the tests, two successive exothermic peaks were observed. The first peak was attributed to the LTO reactions and the second to the coke combustion. A small amount of oxygen contributed to transform to carbon oxides in the first peak. However, most of the oxygen conversion to carbon oxides was related to the second peak, thus the extent of the second peak was believed to be corresponding to the fuel (coke) availability. Results of the RTO tests showed that in the presence of additives, oxidation reactions can happen at a lower temperature and an increased area was observed for the second peak.

Fassihi *et al.* (1984) employed an RTO apparatus in order to gain insight into multiple oxidation reactions occurring during an air injection process, the nature of the fuel, and the impact of distillation and pyrolysis on these reactions. They performed a series of runs on four different oils (10-18 °API) in both isothermal and ramped temperature mode

under a variety of pressure conditions up to 1035 kPa_a. Based on the available literature, which then assumed a minimal effect of interstitial water on fuel availability, no water was added to the oil-sand mixture. The stoichiometric parameters such as hydrogen to carbon atom ratio (H/C) and molar carbon dioxide to carbon oxide ratio (CO₂/CO) were calculated using the effluent gas stream data. These parameters were plotted against temperature to identify the occurring reaction regimes. A linear trend was identified for CO₂/CO ratio when graphed against the natural logarithm of oxygen partial pressure. Also, natural logarithm of the H/C ratio decreased linearly with temperature. A nearly constant value for CO₂/CO molar ratio at high temperatures was interpreted as carbon oxides being produced by the same reaction. By the same token, numerous non-unique reactions at temperatures below 320 °C were implied by varying values of CO₂/CO ratio. An important conclusion in this study was the recognition of possible combustion reactions in the gas phase involving light hydrocarbons produced by distillation and pyrolysis. They defined this class of reactions as medium temperature oxidation reactions (MTO).

Kisler and Shallcross (1997) designed RTO experiments to characterize a 40.2 °API Australian crude oil. They investigated the light oil reaction kinetics, employing a mathematical model (also used by Fassihi, 1984b) which is solely based on oxygen consumption data. The kinetic parameters were calculated by a graphical method, incorporating the experimental RTO data in each of the regimes. Details of this kinetic model are provided in the kinetic models subsection (2.1.2).

In their experiments, which were conducted at a rather low pressure of 700 kPa, the oxygen consumption curves exhibited three peaks. Following the previous works (Fassihi *et al.*, 1984b; Shallcross *et al.*, 1991), they classified the oxidation/combustion reactions into three different and competing regimes of LTO, MTO, and HTO (low,

medium, and high temperature oxidation). MTO was attributed to combustion of “the gaseous light hydrocarbon products of thermal decomposition reactions”. Temperature dependant oxygen combustion curves for heavy oils only feature two peaks. They also observed that more LTO happens for light oils and it results in some carbon oxides production, in contrast to heavy oil LTO. Although the heating rate did not affect the oxidation behavior of the light oil, high pressures resulted in elevated amounts of oxygen consumption in their study.

Moore *et al.* (1999) identified the kinetics behavior of Athabasca oil sands through several experiments performed on the RTO apparatus at the University of Calgary’s In Situ Combustion Research Group (*ISCRG*). This set-up consisted of two identical reactors: an active reactor which replicates the air injection process and a reference reactor which only contains clean core under inert gas injection. The RTO tests clearly showed the transition between LTO and HTO modes through the negative temperature gradient region. The oxygen uptake data for the tests during which only LTO reactions occurred indicated that the residual hydrocarbon after passage of the oxidation front was relatively reactive. High oil production for Athabasca oil was only observed for the RTO tests during which the transition between LTO and HTO modes had been rapid. The gas phase stoichiometric parameters, as indicatives of different operational modes, were consistent with parameter trends obtained from combustion tube tests. They found that the atomic H/C ratio of less than three is associated with an HTO reaction mode.

2.1.2 Reaction kinetic models

In the process of developing a proper and meaningful kinetic model for oxidation/combustion reactions of crude oils, there are essential steps that require adequate knowledge of:

1. crude oil's characteristics and its thermodynamic phase behavior
2. multiple reaction regimes and their dominance over different temperature ranges
3. available mathematical models and their assumptions and simplifications
4. kinetic parameters obtained from fitting quantitative experimental data into the mathematical model

Crude oil is a complex material which consists of numerous components which call for a vast number of kinetic expressions. Since it is not easy to describe all the reactions associated with oxidation/combustion of all components, a comprehensive compositional analysis which can enable the best grouping of the components into proper pseudo components is required. In the primary kinetic modeling attempts for ISC, the crude oil would normally be split into two pseudo components of heavy oil and light oil, which would consist of the heavier and lighter fractions of the oil. Later with HPAI, more groups were devised. Although it is important to lump together the components which show similar combustion behavior, it should be taken into account that thermodynamic phase behavior for light oils is a key definitive factor. Thus, lumping of the oil components needs to satisfy the vaporization phenomenon and the complexity of coupling of kinetics and phase behavior. In other words, since phase change is a dominant mechanism for light oils, and the components participating in oxidation/combustion reactions are influenced by the phase behavior of the oil, it is crucial to look into the lumping procedure with an emphasis on grouping together the components with similar vaporization ranges.

Conventional analysis describes the combustion reaction with a simple reaction rate model of the following form:

$$R_c = -\frac{dC}{dt} = kP_{O_2}^m C_f^n \quad 2.1$$

where, R_c is the combustion reaction rate (gmol/s), k is the Arrhenius reaction rate constant, P_{O_2} is the oxygen partial pressure (kPa), C_f is the concentration of the fuel (gmol/m³), m and n are the reaction orders with respect to oxygen and fuel. Arrhenius constant, k , is defined by the Arrhenius equation:

$$k = Ae^{(-E/RT)} \quad 2.2$$

where, A is the frequency factor (or pre-exponential factor, 1/kPa s), E is the activation energy (J/gmol), R is the universal gas constant (J/gmol K), and T is absolute temperature (K). Equation 2.1 correlates the oxidation reaction rate to temperature through four kinetic parameters, namely frequency factor, activation energy, order of the reaction with respect to oxygen and order of the reaction with respect to fuel. These kinetic parameters are primarily obtained through fitting quantitative experimental data into a mathematical model. A few conventional models exist in the literature; however, development of each model is based on a few simplifying assumptions which adds a source of error and uncertainty. Equation 2.1 is valid under the assumptions of homogenous, elementary reactions. Application of this equation to oxidation reactions of oxygenated compounds, such as combustion of ketones, alcohols, and peroxides, does not satisfy the pre-assumptions. However, this equation is the most widely used equation in kinetic modeling of ISC and HPAI. Researchers have employed different versions of this equation to calculate kinetic parameters based on experimental data.

Bousaid and Ramey (1968) studied the oxidation/combustion reaction kinetics using the experimental results of 48 air injection runs on previously coked samples of 2 different

oils (13.9 °API and 22.1 °API) under isothermal conditions in a combustion cell. The temperature in the combustion runs and coking runs, which were nitrogen injection runs at elevated temperatures, covered a range of 265- 670 °C. Most runs were under atmospheric pressure. However, to study the effect of oxygen partial pressure, some runs were performed at 167 kPa. The effective oxygen partial pressure for each run was calculated from arithmetic average of the inlet and outlet pressures. They assumed that the reaction order with respect to oxygen (m) is unity, and rearranged the reaction rate equation (Equation 2.1) into:

$$\log \left(\frac{-dC}{P_{O_2}} \frac{dt}{dt} \right) = n \log(C) + \log(K) \quad 2.3$$

Plotting the carbon consumption rate against the carbon concentration on a log-log scale would reveal a straight line under constant temperature and constant gas flux. This slope represented the order of reaction with respect to carbon/fuel (m) and was found to be unity in most of the runs, although it varied between 0.6 and 0.9 in a few runs. In order to study the reaction order with respect to oxygen partial pressure they rearranged the reaction order to the form of:

$$\frac{-dC}{C^m} \frac{dt}{dt} = KP_{O_2}^n \quad 2.4$$

When plotting the carbon consumption data against the oxygen partial pressure, it was observed that at all temperature levels a straight line could be fitted into the data, implying a first order dependency on the oxygen partial pressure. Thus, they presented a final form of the reaction rate as:

$$-\frac{dC}{dt} = K C P_{O_2} \quad 2.5$$

The following rearranged form of the Arrhenius reaction rate constant equation yields activation energies and frequency factors at different temperatures.

$$\log(K) = \log(A) - \frac{E}{2.303 RT} \quad 2.6$$

Activation energies reported in the literature for carbon burning range approximately between 44,000 J/gmol and 110,000 J/gmol. However, the values obtained in their study were 57,200 J/gmol for the 13.9 °API oil and 56,500 J/gmol for the 22.1 °API oil, which were very similar and insensitive to the oil gravity. They also investigated the effect of diffusion on the reaction rate at the atmospheric pressure through experiments which were run at different injection fluxes (2.5- 39.6 sm³/m²h). The calculated reaction rate constants showed small or negligible change with gas flux and the reactions seemed to be chemically controlled. However, the combustion cell data at atmospheric pressure do not necessarily mimic the gas diffusion behaviour at combustion tube test or field pressure conditions.

Although Bousaid and Ramey's method is straight forward, it requires isothermal conditions which are not easily achieved during most of the kinetic experiments when exothermic reactions are involved. Fassihi *et al.* (1984) developed a non-isothermal method to obtain the kinetic parameters. This model is under the assumptions of constant molecular weight for the hydrocarbon fuel and unity order of reaction with respect to fuel. The model incorporates the carbon dioxide concentration in the effluent

gas from an RTO test into a “relative reaction rate” term which represents the oxygen consumption rate and is thus proportional to the fuel consumption rate:

$$\frac{q\Delta C_{O_2}}{L} = P_{O_2}^m \quad C_f^n = -\nu \frac{dC_f}{dt} \quad 2.7$$

where, ν is the proportionality factor, equal to the amount of oxygen in moles that reacts with one gram of fuel. Integration between $t=t$ and $t=\infty$ yields:

$$\frac{\Delta C_{O_2}}{\int_t^\infty \Delta C_{O_2} dt'}^{\frac{1}{n}} = \beta \quad 2.8$$

Here, β represents the following group:

$$\beta = \left(\frac{q}{L}\right)^{\frac{n-1}{n}} \frac{P_{O_2}^m}{\nu^n} \quad 2.9$$

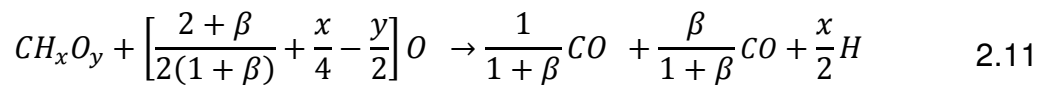
Graphing the left hand side term in Equation 2.8 (relative reaction rate) against inverse temperature yielded a semi-log straight line for high temperature data of their heavy oil RTO tests. From the slope of this line, activation energy could be calculated. At lower temperatures, a departure from the straight line implied that the assumption of constant molecular weight for the fuel or in other words a single reaction model is not adequate to describe the oxidation behaviour at these temperatures.

It was also noted in this study that the chemical reaction step for the experiments were slower than the diffusion step and oxidation/combustion reactions were kinetically controlled. This was concluded based on both calculation of the diffusion rate through correlations and a negligible change in reaction rate constant with a twofold increase in the air injection flux.

Clara *et al.* (1999) proposed a laboratory procedure to evaluate the LOAI (Light Oil Air Injection) recovery potential in HANDIL field, Indonesia. This procedure used five different experiments which were representative of HPAI at reservoir conditions. The Isothermal Disk Reactor Experiment was the specific test that was designed to calculate the kinetic parameters. They adapted a kinetic model which was originally developed at TOTAL's Air Injection Laboratory (Solignac, 1996). This simple kinetic model included a two step oxidation reaction scheme which was also implemented by Mamora *et al.* (1993). In this model oxygen was consumed to produce the oxygenated compounds which would later combust into carbon oxides and water. Formation of oxygenated compounds through the oxygen addition reactions was described by the following form:



Carbon oxides and water were defined to be produced as a result of the bond scission reactions through the following general reaction:



Typical average values for x, y, and β were considered to be as 1.6, 0.5, and 0.05- 0.2 respectively.

Applying the Arrhenius law to these equations gives a set of two equations and eight unknowns, namely two pre-exponential constants, two activation energies, two reaction orders with respect to oxygen and two reaction orders with respect to fuel. If the Arrhenius equation for the combustion equation is rearranged as the following, with A, E,

m, and n (as pre-exponential factor, activation energy, reaction order with respect to oxygen and reaction order with respect to fuel):

$$\ln\left(\frac{dO_2}{dt}\right) = \ln A \cdot CH_xO_y^m - \frac{1}{RT}E + n \ln P_{O_2} \quad 2.12$$

then, if the experiments are run at 3 different temperatures levels, for each reaction a matrix of three equations and three unknowns can be solved to yield these parameters: $\ln A + m \ln CH_xO_y$, E , and n . So, with this method only the activation energies and the orders of reaction with respect to fuel will be obtained. Of course, this methodology is based on the assumption that the concentration of the fuel is constant over the duration of the test, which is a less accurate hypothesis in the case of the oxidation equation which is involved with less stable compounds. Activation energies can be estimated by a simpler method, which assumes a constant oxygen partial pressure suitable only for laboratory experiments. In this method, the Arrhenius equation can be rearranged in this form:

$$\ln\left(\frac{dO_2}{dt}\right) = [\ln A \cdot CH_xO_y^m + n \ln P_{O_2}] - \frac{1}{RT}E \quad 2.13$$

Plotting the natural log of the oxygen consumption rates as a function of inverse of temperature, the activation energy can be estimated through linear interpolation.

Conventional methods of kinetic analysis assume that the form of the kinetic model and reactions are known. The reviewed models so far were based on a power-law mathematical model, similar to Equation 2.1, to represent the dependency of the rate of the reactions to the reactants. Any inconsistency between the model and the real system is reflected as an error in estimated parameters. Cinar *et al.* (2008), pondered on the

question whether the iso-conversional method can be applied to obtain a reaction-free kinetic model to limit the sources of uncertainty. They developed a model-free procedure to find activation energy as a function of conversion. However, the iso-conversional principal assumes that at the same extent of conversion, the reaction rate is only a function of temperature. The rate of fractional conversion, α , was defined as:

$$\frac{d\alpha}{dt} = f(\alpha) \quad 2.14$$

At constant values of conversion, $f(\alpha)$ was assumed to be constant. In other words, the chemistry of the process was assumed to be independent of temperature and heating rate and only dependant on the level of conversion. The iso-conversional method applied to RTO data of Hamaca oil (10.1 °API) showed different activation energies at different conversion levels. This is indicative of different reaction mechanisms dominating at different temperature ranges. The results exhibited around 51000 J/mol of activation energy for HTO reactions. However, results for LTO were not similar in magnitude to be put together as an average value. Activation energy when conversion factor varied between 0.25 and 0.40 was zero, which was the minimum allowed value for the model. This highlights a non-Arrhenius behavior for those conversion levels, which is typically ignored during conventional modeling of oxidation reactions kinetics.

Multiple oxidation/cracking reactions are often assumed for air injection processes. These reaction schemes usually consist of at least one thermal cracking reaction, one or more low temperature oxidation reactions (oxygen addition reactions) and often two or more combustion reactions (bond scission reactions). The classical heavy oil kinetic models consist of three principal types of reactions as follows.

Pyrolysis or Fuel Deposition:

Pyrolysis of crude oil in porous media refers to modification of crude oil by thermal effects in the absence of oxygen. At low temperatures it is called visbreaking or aquathermolysis while at high temperatures it is classified as thermal cracking. In heavy oil combustion literature, it is generally believed that fuel is deposited in liquid and/or solid phase through pyrolysis.

Oxygen Addition Reactions (LTO):

In this type of reactions, also known as low temperature oxidation (LTO) reactions, the oxygen binds chemically with the hydrocarbon molecules and produces oxygenated compounds such as aldehydes, alcohols, ketones and hydroperoxides (Burger and Sahuquet, 1972). Since these products tend to further react and polymerize, operation in the low temperature mode is not favorable. In general, LTO reactions are assumed to occur in the liquid phase; however, there is no reason to eliminate this type of reaction from occurrence in the vapor phase.

Bond Scission Reactions (HTO):

Also known as combustion or high temperature oxidation (HTO), these reactions involve the destructive oxidation of the hydrocarbon to produce carbon oxides and water. It is

noted (Moore *et al.*, 1998) that HTO reactions occur in both the low temperature range ($T < 300\text{ }^{\circ}\text{C}$) and high temperature range ($T > 350\text{ }^{\circ}\text{C}$). In the traditional combustion literature, bond scission reactions are associated with a coke-like fuel; however, these reactions may be homogeneous gas phase reactions or liquid phase reactions involving the oxygen dissolved in the liquid oil or in the water, which is in equilibrium with the oil.

The conventional combustion kinetics involves the complete combustion of a coke-like solid residue as the fuel. Although some authors (Fassihi *et al.*, 1984a ; Kuhlman, 2000; Moore *et al.*, 2008) have suggested the possibility of combustion reactions in the vapor phase, a comprehensive laboratory methodology in order to study the kinetics of this type of oxidation reactions, has not been reported yet.

Thermal cracking has been studied by several authors such as Hayashitani (1978), Vossoughi *et al.* (1982), Fassihi *et al.* (1984), Millour *et al.* (1985), Lin *et al.* (1987) and Abu Khamsin *et al.* (1988). The *In-Situ* Combustion Research Group at the University of Calgary has been investigating the low temperature oxidation reactions during the last thirty years and the findings have been reported in the literature by Adegbesan *et al.* (1982), Belgrave (1987), Millour *et al.* (1987), Moore *et al.* (1992), and Jia *et al.* (2006). Some of these works will be reviewed in the following.

Analyzing the thermograms of a 19.8 °API oil and the effluent gas stream from TGA experiments, Vossoughi *et al.* (1982) realized that distillation and thermal cracking of the crude oil under air flow occur simultaneously with oxidation/combustion reactions. For temperatures below $400\text{ }^{\circ}\text{C}$, the TGA sample weight loss under a nitrogen flow was attributed to distillation. Minor thermal cracking was observed between $400\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$ and again between $550\text{ }^{\circ}\text{C}$ and $900\text{ }^{\circ}\text{C}$ for this oil in the non-oxidizing atmosphere. In order to clarify whether distillation of the medium/heavy components occurs with or after

cracking, an air test was designed where the heating schedule of 10 °C/min was paused at 300 °C for an hour and then was continued to 700 °C. This would allow the components which were distilled up to 300 °C to be removed. The obtained thermograms were then compared to those of an air test, where the sample was heated directly from ambient to 700 °C with the same heating rate. The difference between the fractional weight loss rates indicated by the thermograms was attributed to those components which distilled simultaneously with the oxidation reactions. It was also realized that distillation is essentially complete before the final stage of reactions which were the combustion of the residual coke.

Effluent gas analysis between 385 °C and 500 °C revealed that only 33.5% of the weight loss during this temperature range was due to CO₂ and H₂O production and the remaining weight loss corresponded to distillation and thermal cracking of the medium/heavy components into the light, more volatile components. Thus, it highlighted the possibility of parallel occurrence of the combustion and distillation/cracking reactions in an oxidizing atmosphere.

Lin et al. (1987) presented a modified kinetic model for thermal cracking of the crude oil. They added one cracking reaction to the widely used cracking reaction scheme. This inclusion was to allow the lighter fraction of the crude oil ("intermediate products") to participate in the cracking reactions which lead to formation of coke. The typical reaction order used for thermal cracking of the crude oil is unity; however, Lin *et al.* suggested that the value should be greater than one. Since a heavy oil pseudo component's constituents do not react at the same rate, the composition of the oil will change with time. In order to meet this compositional effect, also known as depth-of-cracking effect, they added a correction factor to the rate equation in the form of $\left(\frac{C}{C_i}\right)^{n(T)}$, where C_i

referred to the initial composition of the reactant. The rate equation would then be modified to the form of:

$$-\frac{dC}{dt} = K \left(\frac{C}{C_i} \right)^{n(T)} C \quad 2.18$$

Based on analysis of the experimental data, they suggested an exponential dependency of n to temperature. The correlation included parameters a and b which are characteristics of the crude oil system. Equation 2.8 describes the suggested form which implies that the apparent order of the reaction decreases with temperature.

$$n(T) = a - b \quad 2.19$$

Lin *et al.* further emphasized the procedure for lumping of the crude oil into pseudo-components due to its impact on simulating the vaporization phenomenon and its consequent compositional effects and recommended phase-behavior based considerations.

Belgrave *et al.* (1993) proposed a kinetic model which included oxygen addition reactions, in addition to thermal crackings, as fuel generating reactions for the combustion zone. This model combined the data from experimental kinetic studies of Hayashitani (1978) for thermal cracking reactions and Adegbesan (1982) for oxygen addition reactions. The model assumed a reaction order of unity with respect to both oxygen and coke. Their proposed scheme for cracking reactions (with stoichiometric coefficients expressed in terms of moles) included:

Maltenes $\rightarrow$ 0.372 Asphaltenes

Asphaltenes → 82.223 *Coke*

Asphaltenes → 37.683 *Gas*

Oxygen addition reaction equations were defined as:

Maltenes + 3.431 *Oxygen* → 0.4726 *Asphaltenes*

Asphaltenes + 7.513 *Oxygen* → 101.539 *Coke*

The stoichiometric coefficients for these equations were calculated using the estimated molecular weight of the pseudo components and the oxygen addition reactions' uptake ratios. The developed kinetic model was used to simulate the results of one RTO and two combustion tube (dry forward and super wet) tests. The model could predict the experimentally determined frontal velocity and oxygen and fuel requirements in addition to dual oxidation uptake peaks and coke delay associated with RTO tests. This model proved that the thermal cracking reactions, in isolation, do not generate sufficient fuel for combustion reactions and oxygen addition reactions are the dominant mechanism for fuel generation in ISC process.

Moore *et al.* (1992) performed several RTO experiments on Athabasca oil sands under various air injection fluxes, initial fluid saturations, and heating schedules to study the mechanisms associated with bond scission and oxygen addition reactions over high temperature and low temperature oxidation/combustion regions respectively. The observations led to expansive findings on the kinetics of in situ combustion, the most important perhaps being the recognition of the negative temperature gradient region. This is referred to the low reaction rate region, where oxygen uptake and energy generation decrease with increasing temperature and this behaviour is observed at the

intermediate temperatures between the typical low and high temperature oxidation regions.

Drawing on Belgrave *et al.*'s (1990) demonstration of how the oxidation behavior of an oil can be described by a two component system: maltenes and asphaltenes, Moore *et al.* (1992) argued that at lower temperatures the more reactive oil fraction (maltenes) consumes the oxygen preferentially and thus increases the asphaltene fraction of the oil. They discussed that oxidation of the asphaltenes is a slow process at low temperatures and this becomes the onset of the low reaction rate region. While oxidation rates within the high temperature combustion zone are controlled by the rate of delivery of oxygen in an RTO test, low temperature oxidation reactions are limited to the rate of diffusion of oxygen to the reactive hydrocarbon phase. Fouling of the reaction surface and thus oxygen starvation of the reaction zone prevents the reactions to switch to a desired combustion mode and the global kinetics switch into a mass transfer controlled mode.

2.2 Numerical Simulation of HPAI

Most of the rigorous first generation in-situ combustion simulators were developed around the years 1975-1985 (Farouq Ali, 1977; Crookston *et al.*, 1979; Grabowski *et al.*, 1979; Coats, 1980; Youngren, 1980; Rubin and Buchanan, 1985).

Lin *et al.* (1984) studied the process mechanisms and fuel availability using a thermal simulator developed by Crookston *et al.* (1979). They split the oil into two pseudo components (light and heavy) and employed four reactions: one cracking reaction for the heavy pseudo component to form light oil and coke and three combustion reactions for light oil, heavy oil, and coke. Details of the reaction scheme are shown in Table 2.1.

The phase equilibrium K-values were generated using an equation of state based on initial compositions of the pseudo components. Since this procedure did not account for

compositional changes, the obtained K-values were allowed to be adjusted during the history matching to implicitly account for compositional changes.

A sensitivity analysis showed that the simulation results were sensitive to the K-values of the light oil component for both the medium-weight oil (A) and heavy oil (B) that were studied. For oil A (peak temperature 482 °C) coke formed only 21% of the burnt fuel and the results of simulation were not sensitive to the kinetics of the cracking reaction. However for the heavy oil B (peak temperature 760 °C), coke was the only source of fuel and the fuel deposition mechanism was sensitive to the kinetics of the cracking reaction. The first order Arrhenius based oxidation reaction rates that were implemented for this study did not impose any sensitivity to the simulation results under conditions of the studied system.

Kumar (1987) used the laboratory combustion tube data of a 26 °API crude oil to validate a fully implicit thermal simulator (ISCOM, by Computer Modeling Group) and also to study some important input parameters that affected the predicted results. He characterized the oil into three pseudo components of heavy oil, light oil, and coke and defined two cracking reactions and three combustion reactions (Table 2.1). Although measured cracking rates were used in this study, the stoichiometric and reaction parameters were used as adjustable parameters during history matching stage. However, the simulation results were insensitive to the kinetics of combustion reactions and the advance of the combustion front was controlled by the air injection. The velocity of the oxidation/combustion front was proportional to air flux.

The non-compositional equilibrium K-values for this study were adopted from Lin *et al.* (1984); however, Kumar performed a sensitivity analysis on this parameter for both heavy and light components. While decreasing the K-value of the heavy component

imposed a small effect on the results of the simulation, increasing the K-value led to more vaporization of the heavy component which led to lower coke formation. A decrease in the K-value of the light oil component proved to have the highest impact on the predicted results. A 20% reduction in K-value caused the fuel consumption to increase and the coke fraction of the fuel to increase from 8.5% to 13%. These resulted in higher peak temperatures and a lower rate of advance for the oxidation/combustion front. Kumar's analysis also showed that the predicted results were sensitive to the relative permeability and capillary pressure near the irreducible water saturation.

Fassihi (1992) studied the effect of compositional K-values on the simulation results of flue gas and air injection experiments on a 35 °API light oil. The phase behavior of this oil was described by five pure component, N_2 , CO_2 , C_1 , C_2 , C_3 , and seven pseudo components, namely C_4 , C_{5-6} , C_{7-10} , C_{11-15} , C_{16-21} , C_{22-29} , and C_{30}^+ . In this study, the compositional K-values obtained by EOS, showed a correlation with the composition of CO_2 in the liquid phase. The developed correlation was then used in a flue gas injection model, where K-values were allowed to be a function of pressure, temperature and also the composition of one component in either liquid or gas phase. The cumulative oil production and GOR calculated by this model were in good agreement with the results of the EOS compositional model, except at the front and back ends of the compositional path during the displacement process.

A one dimensional air injection simulation was conducted in this study. Since the oxidation reaction was only allowed for the heaviest components (C_{16}^+) and the lighter components were assumed to vaporize and produce ahead of the combustion front, the results showed similar behavior between the flue gas and air injection simulations and in this paper, it was concluded that "air injection is essentially a flue gas generator in light oil reservoirs."

Tingas *et al.* (1996) investigated the feasibility of the high pressure air injection process in North Sea type light oil reservoirs. They examined the process through field-scale simulations, based on a pseudo compositional model using CMG STARS. The accuracy of these light oil models were supported by detailed phase behavior characterization of the fluids based on equation of state. The results of this study highlighted the mass transfer between phases and oil vaporization as two of the important processes in this thermal recovery method. In their simulation runs, no temperature dependency of relative permeability or capillary pressure was considered. Also the effect of hysteresis on relative permeabilities was neglected. Final relative permeability curves were determined from history matching of the oxygen consumption, recovery, and flue gas breakthrough in combustion tube tests.

Tingas *et al.* characterized the light oil by 3 pseudo-components, CH_4 , C_{2-6} , and C_7^+ (overall 9 components for the simulation model). The description is presented in Table (2.1). The component K-values were calculated by Standing's correlation, Wilson's correlation, and also through an equation of state. But, they concluded that the EOS based K-values were more appropriate for high pressure light oil reservoirs. The simulation results were more sensitive to the K-values of the light components compared to the heavy components.

The chemical reactions defined in their study consisted of heavy fraction cracking, and heavy fraction, light fraction, gas (CH_4), and coke combustion. The stoichiometric calculations were based on an assumption of 1.6 for the value of H/C ratio. The CO_2/CO ratios were matched to combustion tube tests' data, through adjusting the kinetic parameters.

Both kinetics of cracking reactions and light component equilibrium K-values were found to be the most important factors in fuel deposition mechanism and fuel composition. Basically, their simulation results proved compositional effects to be very important and definitive in HPAI processes, especially for North Sea type oil which needed at least a 4 pseudo-component characterization for an accurate representation in the simulation model.

They reported that the development of the combustion front including its velocity can only be accurately predicted for field simulations of high density wells. For a North Sea typical reservoir of 120 acre well spacing, an 11% incremental recovery was predicted for a post water-flood HPAI process.

Fassihi *et al.* (2000) conducted a laboratory and simulation study in order to characterize the reaction scheme for the West Hackberry light oil air injection process and evaluate the air injection suitability in West Hackberry field, Louisiana. Core flood and combustion tube tests were performed on a 32.7 °API oil and the tests were modeled employing a compositional simulator. Results of these simulation studies were further used in a thermal compositional simulator for the field scale air injection study.

A comprehensive phase behavior description, based on equation of state was employed to estimate the K-values and fluid properties. This phase behavior model used the data from PVT laboratory experiments performed on the mixture of a flue gas and the recombined oil. The K-value estimation procedure was a continuation of Fassihi's previous work (1992). The K-values were cross-correlated against the mole fraction of nitrogen in the oil phase and were presented as a function of pressure, temperature and nitrogen composition. The effluent composition resulted from the core-flood simulations

showed close agreement with the experimental results. This indicated the successful capturing of the vaporization phenomenon by the composition-based K-values.

In simulation of the air injection tests, six reactions were defined: two cracking, three liquid phase combustion, and one coke combustion reaction (details in Table 2.1). The authors believed that due to their high activation energies, the cracking reactions played a minimal role in the history matching stage and the amount of coke formed was insignificant. The reaction order with respect to fuel was set to 2 for a stable computation and also the pre-exponential factor had to be adjusted so as to match the oxygen content of the effluent gas.

Kuhlman (2000) studied the performance of the HPAI through simulation of the process in two mechanistically different reservoir models: a viscous-dominated and a gravity-stable model. He evaluated black oil (IMEX), thermal (STARS), and EOS (GEM) simulators from Computer Modelling Group (CMG) for each case. Reservoir bubble point gas, air, and flue gas were the injection gases, respectively. The phase behavior data were generated by CMG WINPROP for a 32 °API alkane distribution. The gas compositions were set as adjustable parameters in the regression stage to match the oil properties at the bubble point. However, it is not clear what K-values were used in this study. Ten hydrocarbon pseudo components were used in the EOS model and six were defined for the thermal model (Table 2.1). The paper does not emphasize the thermal effects of the oxidation/combustion front and thus does not necessarily consider the process as a thermal process. It is stated in the paper that “clearly, light oil air injection is really a cold process, but thermal effects can be important.” Therefore as one of the results of this work, thermal simulation is recommended for all conditions except for hot thick reservoirs where, in the author’s opinion, EOS model would be a better option. Kuhlman further discussed that since the DSC and ARC tests for light oils normally show

that the onset of HPAI reactions coincide with the vaporization of the mid-range hydrocarbons, the C₈₋₁₇ and C₁₈₋₂₉ components were allowed to react in the vapor phase, and were modeled as a first order reaction of oxygen and hydrocarbon.

Kristensen *et al.* (2008) emphasized the importance of phase behavior description, equilibrium K-values in particular, through a simulation study which employed an equation of state based in situ combustion simulator, VCT (virtual Combustion Tube), which was developed by Kristensen (2008). Previous ISC models (Crookston *et al.*, 1979; Grabowski *et al.*, 1979; Coats, 1980) and CMG (2004) took the K-value based approach for description of phase behavior, where K-values often were only dependant on pressure and temperature. In their work, Kristensen *et al.* compared the EOS and K-value based phase behavior approaches. The K-value based approach further consisted of two different methodologies: K-values from Wilson correlation (Michelsen and Mollerup, 2004) and optimized K-values (tabulated K-values from EOS flashes of the initial oil at different pressures and temperatures). The results of the ISC simulations in VCT simulator showed that for a particular ignition setting, the critical air requirement for sustaining the combustion is up to 17% different between two models, being overestimated by the optimized K-value approach. Kristensen *et al.* recognized that lighter oils are intuitively more sensitive to the phase behavior description and the assumption of combustion being only in the oil phase is “questionable”.

Moore *et al.* (2009) have described the challenges associated with the prediction of field performance of air injection processes using numerical and laboratory models. In this paper, the major common misinterpretations and simplifications used by reservoir engineers to model the process are addressed. These simplified models generally lead to wrong predictions of the field performance in terms of the oxidation/combustion behavior and in some cases are critical enough to result in a failure. Their paper

highlights the importance of the amount of the fuel, the nature of the fuel, the role of relative permeability curves, and the role of the heaters and radial heat losses in history matching of the combustion tube tests. It also clarifies how some concepts like spontaneous ignition and some factors like reaction kinetic parameters are inherent challenges to the numerical modelling of ISC and HPAI processes due to lack of complete understanding of the combustion processes. New features in thermal reservoir simulators for avoiding some of the potential pitfalls were also highlighted. The authors believe that “the prediction of field performance of air injection projects is a difficult task for which there are still more questions and uncertainties than definitive answers”

Table 2-1 A summary of some main reaction kinetic models in the literature

Year	Authors	Reactant	Reactions*	Pre-exponential factor	Activation Energy	Enthalpy	K-values	Simulator
1884	Lin <i>et al.</i>	26.5 °API	HO → 3.65 LO + 1.91 Coke LO + 13 O ₂ → 10 COx + 9.6 H ₂ O HO + 59 O ₂ → 48 COx + 43.5 H ₂ O Coke + 1.15 O ₂ → COx + 0.5 H ₂ O				created by EOS, adjusted implicitly during history match	crookston; semi implicit
1987	Kumar	26 °API	HO → 3.71 LO + 7.13 Coke LO → 11.96 Coke HO + 56.99 O ₂ → 51.53 COx + 28.34 H ₂ O LO + 13.23 O ₂ → 11.96 COx + 6.58 H ₂ O Coke + 1.11 O ₂ → COx + .55 H ₂ O	1.73E12 (h ⁻¹) 2.1E9 (h ⁻¹) 3.02E10 (h ⁻¹ psi ⁻¹) 3.02E10 (h ⁻¹ psi ⁻¹) 4.17E4 (h ⁻¹ psi ⁻¹)	72910 (Btu/lb-mole) 64460 (Btu/lb-mole) 59450 (Btu/lb-mole) 59450 (Btu/lb-mole) 25200 (Btu/lb-mole)		Tabulated K-values from Lin <i>et al.</i>	ISCOM by CMG; fully implicit
1996	Tingas <i>et al.</i>	North Sea Volatile Light Oil	C ₇₊ → 0.2 C ₂₋₆ + 13.75 Coke C ₇₊ → 0.6 CH ₄ + 13.75 Coke Coke + 0.9 O ₂ → 0.8 H ₂ O + CO C ₇₊ + 13.13 O ₂ → 11.87 H ₂ O + 14.4 CO C ₂₋₆ + 3.68 O ₂ → 4.25 H ₂ O + 3.11 CO CH ₄ + 1.5 O ₂ → 2 H ₂ O + CO CO + 0.5 O ₂ → CO ₂		33300 (Btu/lb-mole) 27000 (Btu/lb-mole) 25200 (Btu/lb-mole) 33300 (Btu/lb-mole) 33300 (Btu/lb-mole) 59450 (Btu/lb-mole) adjusted for CO ₂ /CO	0 0 225000 (Btu/lb-mole) 4740000 (Btu/lb-mole) 9000000 (Btu/lb-mole) 12500000 (Btu/lb-mole) adjusted for CO ₂ /CO	Standing's correlation, Wilson's correlation, and also through an equation of state	STARS by CMG
2000	Fassihi <i>et al.</i>	32.7 °API	C ₁₂₋₁₇ → 0.6663 Coke + 1.5276 C ₇₋₁₁ C ₁₈₊ → 1.255 Coke + 2.8774 C ₇₋₁₁ C ₇₋₁₁ + 12.062 O ₂ → 8.541 CO ₂ + 7.145 H ₂ O C ₁₂₋₁₇ + 19.395 O ₂ → 13.734 CO ₂ + 11.488 H ₂ O C ₁₈₊ + 36.535 O ₂ → 25.871 CO ₂ + 21.639 H ₂ O Coke + 1.455 O ₂ → 1.0 CO ₂ + 0.9366 H ₂ O	3.3521E10 (h ⁻¹) 3.3521E10 (h ⁻¹) 4.0E10 (h ⁻¹ psi ⁻²) 4.0E10 (h ⁻¹ psi ⁻²) 4.0E10 (h ⁻¹ psi ⁻²) 1.0E8 (h ⁻¹ psi ⁻²)	77435 (Btu/lb-mole) 77435 (Btu/lb-mole) 48600 (Btu/lb-mole) 48600 (Btu/lb-mole) 48600 (Btu/lb-mole) 14967 (Btu/lb-mole)	0 (kcal/ g-mole of O ₂) 0 (kcal/ g-mole of O ₂) 100 (kcal/ g-mole of O ₂) 100 (kcal/ g-mole of O ₂) 100 (kcal/ g-mole of O ₂) 100 (kcal/ g-mole of O ₂)	tabulated K-values based on T,P, and correlated against composition of nitrogen in the liquid phase	STARS by CMG
2000	Kuhlman <i>et al.</i>	32 °API	C ₈₋₁₇ + 16.66 O ₂ → 10.54 H ₂ O + 11.39 CO ₂ C ₁₈₋₃₄ + 35.86 O ₂ → 29.8 H ₂ O + 24.47 CO ₂ C ₃₄₊ + 79.92 O ₂ → 30.77 H ₂ O + 61.54 CO ₂ C ₃₄₊ → 2.386 C ₁₈₋₃₄	2500000 (day ⁻¹) 2.5E6 (day ⁻¹) 1E6 (day ⁻¹) 1E7 (day ⁻¹)	18610 (kcal/g-mole) 18055 (kcal/g-mole) 25000 (kcal/g-mole) 26388 (kcal/g-mole)		not reported	STARS by CMG

* Reaction stoichiometric coefficients are expressed in terms of moles.

Chapter Three: Laboratory Methodology

For the purpose of light oil kinetic studies in this research with an emphasis on the mechanisms associated with flow, most importantly distillation, the RTO (Ramped Temperature Oxidation) type test was found to be appropriate. However for the tests to represent the actual conditions of the light oil fields, a high pressure RTO design was required. Therefore a one dimensional tubular reactor, capable of operation under pressures as high as 6000 psi (41 MPa) was fabricated. This HPRTTO (High Pressure Ramped Temperature Oxidation) reactor captures the overall distillation and oxidation behavior of a light oil by physically simulating the HPAI process under either a predefined heating rate schedule or at a fixed temperature (isothermal operation) at reservoir pressure conditions.

3.1 Description of the Apparatus

The tubular reactor (Figure 3-1) is constructed from nominal one inch (25.4 mm) type 316L stainless steel tubing with 23.6 mm inside diameter and 464 mm of inside length. The reactor is equipped with seven internal Inconel-sheathed thermocouples (ISA Type K, 3.175 mm diameter) with an axial spacing of 57.2 mm. Heat is provided by six metal-clad heaters wound around the outer wall of a machined copper mandrel. Each heater has an output of 2 kW at 208 V. Five thermocouples are mounted on the wall of the copper mandrel to control the heater temperature and one thermocouple serves for estimating axial heat loss, and is silver soldered on the end cap of the reactor (Figure 3-2). The tubular reactor and heating mandrel are mounted inside a pressure jacket which is fabricated from P-110 casing (Figure 3-3). The pressure jacket is fitted with slide-in end caps secured in place using external threaded caps. Sealing between the sliding end caps and pressure jacket is achieved with two sets of Viton O-rings and a flat metal gasket.

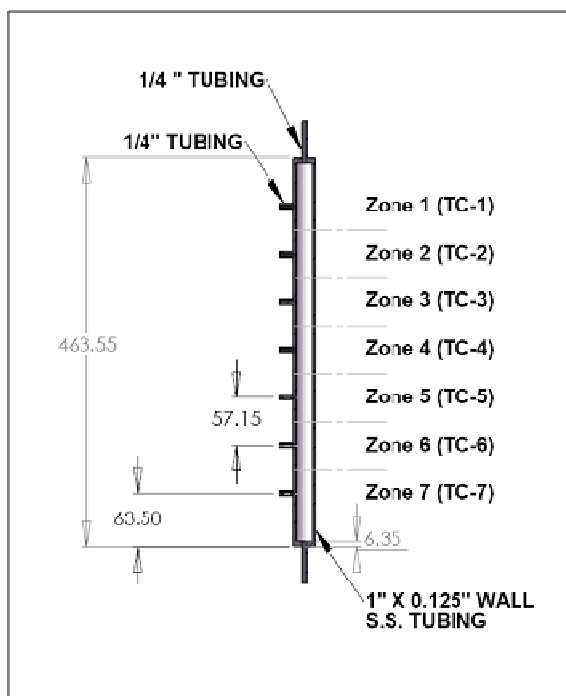


Figure 3-1: Cross sectional view of the HPRTO reactor (lengths in mm)

A mass flow controller (Brooks Instrument Model 5850) was used to control the rate of flow of gas into the reactor. The maximum operation flow rate of the mass flow meter was 60 sl/h and flow was controlled by Brooks Control Module Model 0152. A TESCOM Model 26-1762-24 back pressure regulator was placed at the exit line from the reactor and maintained the desired pressure. The injected gas flowed in a downward direction. Composition of the production gas was analyzed by two Agilent Technologies Model 6890N Network Gas Chromatograph systems on 20 minute cycles and stored on a computer for subsequent analysis. A Ritter Type TG1/5 rotary wet test meter provided a cumulative reading of volumetric flow of the exit gas stream. This wet test meter operates between 2 and 120 l/h flow rates.

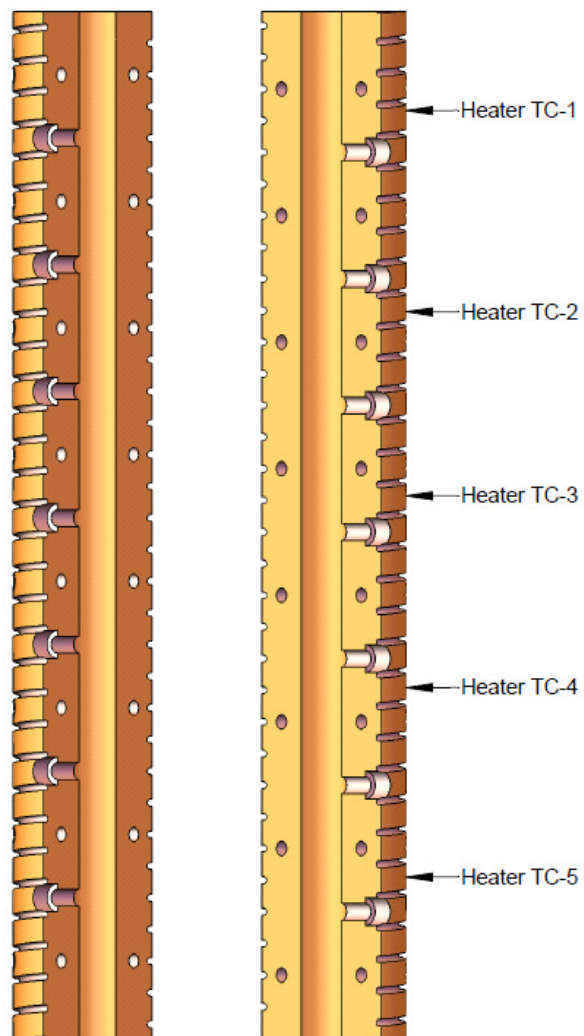
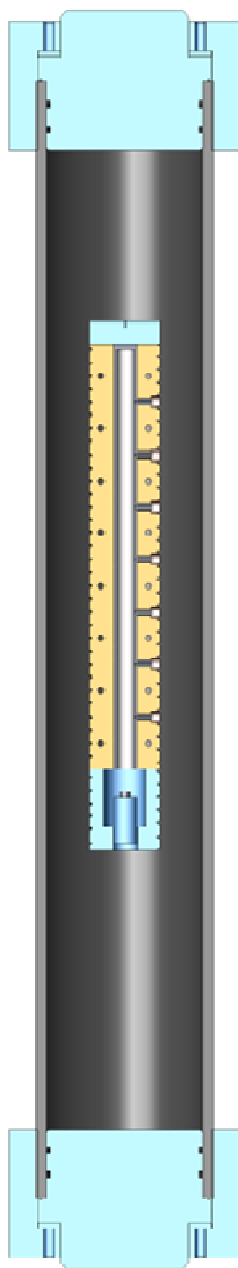


Figure 3-2: Cross sectional view of the copper mandrel



**Figure 3-3: Cross sectional view of the pressure jacket, enclosing the tubular
HPRT reactor**

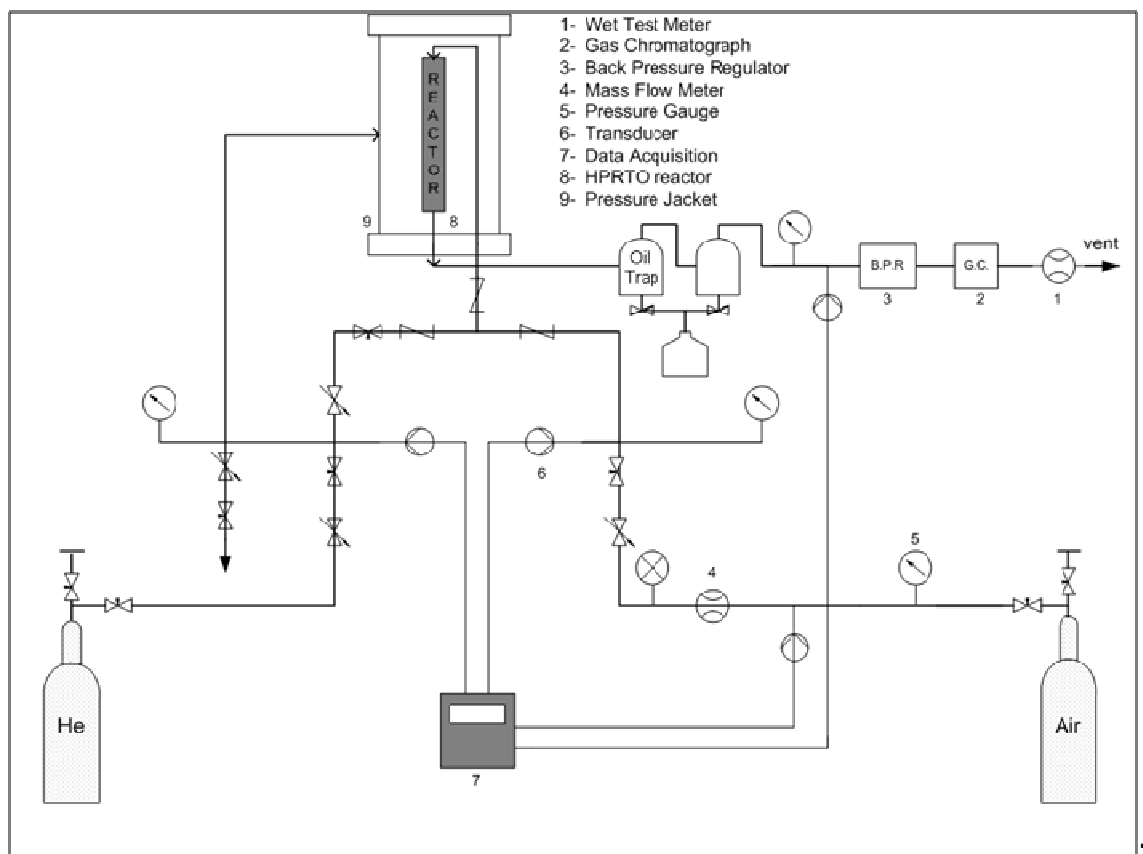


Figure 3-4: Flow diagram of the HPRTO design

A LabView™ data acquisition and heater control system was used to control the reactor heating and record the reactor and heater temperatures along with the pressure, heating rate, and wet test meter data. Other parameters measured during an RTO test include the produced gas composition using gas chromatography, and the produced liquids composition using simulated distillation, as well as the post- test residual hydrocarbon amount and composition. Figure 3-4 depicts the flow diagram of the high-pressure ramped-temperature oxidation set up.

3.2 Hydrocarbon Sample

Two hydrocarbon samples were used for the purpose of this study: a light oil (Oil A) and a pure hydrocarbon ($n\text{-C}_{15}\text{H}_{32}$). Oil A is a 37 °API paraffinic crude oil with a pour point above room temperature. This light oil is from a high pressure and high temperature offshore reservoir. The waxy nature of Oil A is inherent to the paraffin content of the oil. Based on properties presented and the classification of McCain (1990), Oil A is a light black oil. The pure hydrocarbon, normal Pentadecane ($n\text{-C}_{15}\text{H}_{32}$), has the highest concentration among the hydrocarbon components of this selected light oil and was considered for HPRT tests as a pure hydrocarbon component which may exhibit similar characteristics to Oil A. Figure 3-5 shows the distribution of the single carbon number (SCN) hydrocarbon components of Oil A as obtained from simulated distillation.

A PVT and swelling study was completed on a recombined sample of reservoir fluid in an outside lab. The reservoir temperature of Oil A is 116 °C and the initial pressure of this reservoir is 15.8 MPa. Table 3.1 summarizes the major fluid properties of recombined Oil A at reservoir conditions, obtained from PVT tests.

3.3 Porous Media Preparation

All the HPRT tests were performed with samples of unconsolidated carbonate rock which were original reservoir rocks provided from the field of interest. This field is a high pressure off shore reservoir with potential for the HPAL recovery method. The stock tank oil sample used in this study (Oil A) was also obtained from this field. The reservoir rock was crushed, sieved, and dried in an oven at 350 °C for 16 hours. A mixture of reservoir core, oil and/or synthetic brine in specified proportions was prepared and packed in the reactor. The porosity of this system was 40%, on average, and permeabilities in the order of 4 Darcy are achieved. Fifty grams of 16 mesh unsaturated silica sand was placed at the inlet end of the reactor and the pre-mixed core was then tamped into the

reactor while the last inch of the outlet end of the reactor was filled up with another layer of silica sand. This was to prevent the saturated carbonate mix from entering the injection and production lines. Following packing, the reactor was sealed, the copper mandrel was assembled and the thermocouples were installed. After testing for leaks, the apparatus was placed vertically in the pressure jacket with the reactor inlet at the top and was connected to the flow and measurement systems.

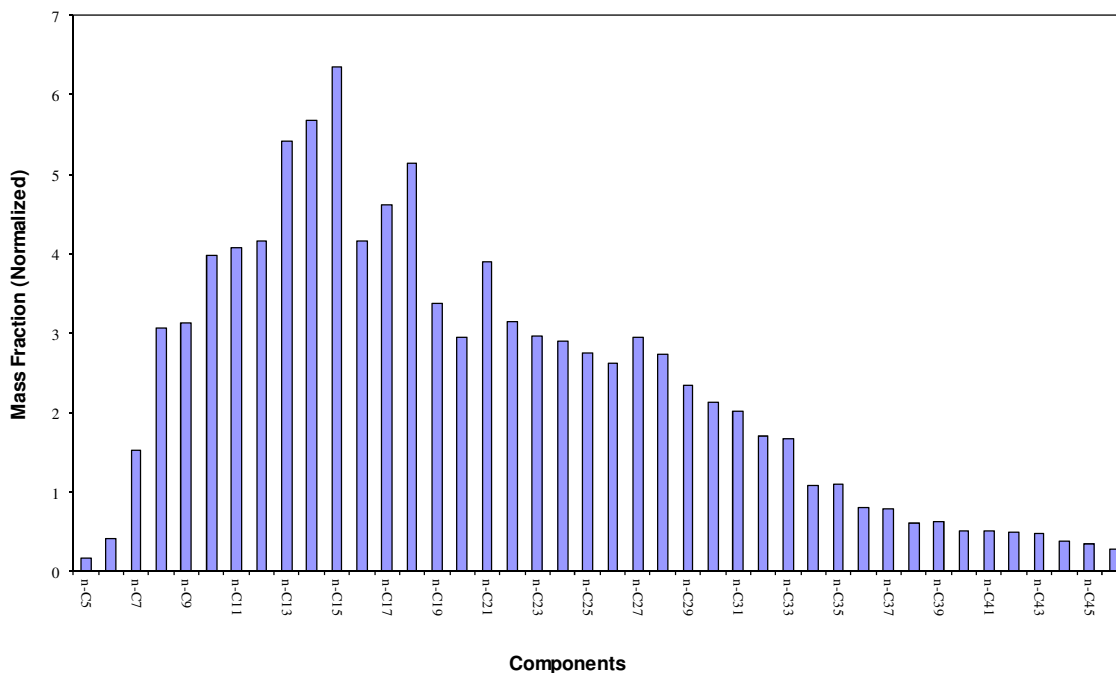


Figure 3-5: Single Carbon Number (SCN) distribution of Oil A, obtained by simulated distillation. n-C₄₆⁺ detected by the Gas Chromatograph were nearly zero.

Table 3.1: Fluid properties of recombined oil A at reservoir conditions

Gas-Oil Ratio		
Single stage flash		73.9 sm^3/sm^3
Total differential liberation		76.8 sm^3/sm^3
Total (3 stage) separator flash		67.1 sm^3/sm^3
API Gravity (at 15 °C)		
Single stage STO		36.0 °API
Differential liberation STO		35.7 °API
Separator STO		37.0 °API
Properties at Reservoir Condition		
Viscosity		0.54 cP
Compressibility (Co)		170E-6 cm^3/kg
Density		0.679 g/cm^3
Formation Volume Factor*		
Single stage flash		1.317
Differential liberation		1.323
Three stage separator		1.288

Table 3.2: Paraffin, naphtene, and aromatic distribution of stock tank Oil A

	Liquid Volume %
Paraffins	49.3
Naphthenes	22.8
Aromatics	27.9
<u><i>Naphtene Distribution</i></u>	
1 Ring	14.3
2 Ring	7.2
3 Ring	0.9
4 Ring	0.0
5 Ring	0.1
6 Ring	0.3
<u><i>Aromatic Distribution</i></u>	
Monoaromatics	15.3
AlkylBenzene	12.0
NaphteneBenzenes	1.7
DinaphteneBenzenes	1.6
Diaromatics	11.5
Naphtalenes	7.7
Acenaphthenes/Dibenzofurans	2.1
Fluorenes	1.7
Triaromatics	0.6
Phenenanthrenes	0.6
Naphthenephenanthrenes	0.0
Tetraaromatics	0.1
Pyrenes	0.1
Chyrsenes	0.0
Pentaaromatics	0.0
Perylenes	0.0
Dibenzathracenes	0.0
Thiopheno Aromatics	0.2
Benzothiophenes	0.2
Dibenzothiophenes	0.0
Naphthabenzothiophenes	0.0
Unidentified Aromatics	0.2

Table 3.3: Stock tank Oil A properties

Density (g/cm ³)	0.8207 @ 23 °C
	0.8114 @ 40 °C
	0.8042 @ 50 °C
	0.7909 @ 65 °C
Viscosity (cP)	4.20 @ 35 °C
	2.94 @ 40 °C
Asphaltenes (% by mass)	0.16
Specific Gravity (@ 15 °C)	0.8265 (39.7 °API)
Molecular Weight (g/mol)	200.9
	(by freezing point depression)
	214.85 (by simulated distillation)

3.4 Experimental Procedure

Once the reactor was packed and secured inside the enclosing pressure jacket, it was pressurized with helium while the annular space between the reactor and the jacket was also simultaneously pressurized with helium to bring the whole system up to representative reservoir pressure. The heating schedule was then defined for the controllers through the computer as per the design of each individual test. The typical slow heating rates used for RTO reactors (40-60 °C/hour) enables the approximation of

the spontaneous ignition phenomenon. All the 15 tests carried out for the purpose of this research were conducted on a ramped temperature mode, except Test 5, which was an isothermal test at the reservoir temperature. Amongst the 14 tests that were performed under the increasing temperature conditions, Test 1 and Test 2 were started at room temperature while the rest of the experiments went through a primary preheating stage. For these tests, the whole reactor system was heated up to a desired temperature (usually 150 °C) in order to limit the oxygen addition reactions at low temperatures. This preheating stage was manually imposed after pressurization and before air injection, i.e. under helium at reservoir pressure. Once at the desired start-off temperature, the heat controllers were switched from manual to ramp/soak mode and flow of the injection gas through the reactor was started at the desired flux. Most tests were performed under the flux of 38.22 sm³/m²h, while for Test 6, Test 7, and Test 15 the flux was lowered by a factor of three to study the low flux conditions.

Nitrogen and air were used as injection gases for different tests to replicate the proper conditions for studying the mechanisms involved with distillation and oxidation/combustion reactions, respectively. Nitrogen forms 85-90% of the effluent gas produced in air injection tests and was chosen to enable the physical simulation of the vaporization phenomenon during the air injection tests.

After a vaporization and/or combustion front had formed and traversed all the thermocouple locations inside the reactor, which usually was just below the temperature set point, the gas flow was terminated, the heaters were turned off and the reactor was allowed to cool down while the whole system was under a slow depressurization. The reactor and the annulus were depressurized through separate lines, although they were pressurized simultaneously. Depressurization of the helium filled annulus through a different line would prevent the flow of helium through the reactor. Normally some small

amount of production occurred during the depressurization stage due to liquid trapped in the pores or the production line. However the major amount of produced oil and water was collected during the test, after formation of a front. The produced oil and water vapors did not get a chance to distil inside the reactor, due to the whole system being kept at the same temperature. Thus, the vapor would later cool down in the production line and be collected as liquid in the production traps. The effluent gas would pass through the traps and the back pressure regulator. A sample of the effluent was then collected and analyzed by the Gas Chromatograph (GC) for its constituents. The GC data were recorded on a computer for further analysis. The volume of the effluent was measured by a wet test meter downstream of the back pressure controller.

3.5 Production System

The production system for the HPRTTO design was modified twice in the course of the research. Primarily the collection system consisted of two “hot” and “cold” separators. The produced fluids would enter the first high pressure collector trap through a dip tube going half way down through the vessel. The temperature of this vessel was kept at 60 °C while the pressure was the same as the whole reactor system. Heating of this trap was achieved by ¾ inches wide silicone heaters wrapped around the vessel and operated by a manual variac. The distilled liquid would separate and drip to the bottom of the vessel while the gas and vapors would rise to the top of the vessel, where they were led to a second cold trap through a line. The temperature of the cold trap was maintained at 0 °C, by locating it in a big container filled with ice. The production from the cold trap was usually minimal. The high pressure separated liquid in the first trap was collected in a jar at different times during the test. This would enable detection of the amount and nature of the produced fluids with time; however, since the produced fluids were collected by opening the valve located at the bottom of the separator vessel,

containing hot and pressurized fluids, some of the production was lost as vapor or even liquid droplets. This was later recognized to impose a large error on the mass balance calculations, since the initial amount of liquids packed inside the reactor were of low quantities, typically around 10-15 grams of water and oil. Therefore, it was recognized that collection at different times was not a proper practice and it was consequently stopped. So, in a newer procedure it was allowed for the produced fluids to be held in the separator vessel for the duration of the test and the vessel would be removed from the system only at the end of the test for collecting and analysing of the liquids. Although this method would spare the loss of liquids during several valve openings, it would not allow the identifying of the production path. This production method was used for Tests 7, 8, 9, 10, and 11 before it was modified for Test 12.

The final design for Test 12 encompassed the practicality of the original method (in terms of emphasizing the path of production) and precision of the second method. It consisted of four container cups, all enclosed by the same vessel. Each of the containers was connected to the main production line with a separate line and valve. Therefore, disconnecting one cup and switching to the next cup during the test would let collection of the produced liquids at four desired time periods, selected according to the temperature response of the individual tests. Usually the last cup was saved for the depressurization step, to prevent the loss of lighter oil fractions that would be stripped by the gas stream.

3.6 Post Test Analysis

The produced fluids and also the unproduced fluids extracted from the post-test core were separated and analyzed in a chemistry laboratory. The mixture of produced water and oil was first centrifuged to obtain clean, intact oil sample for further density, viscosity and simulated distillation analysis. Settings for the centrifuge system were different

depending on the nature of the mixture. When the paraffinic Oil A was involved, the centrifuge was set at 2700 rpm at 40 °C for an hour, while for the more volatile pure pentadecane sample, the 2000 rpm setting at 10 °C for 30 minutes was enough to yield a clean oil phase at the top which would later be removed for further analysis. The remainder of the fluids which contained some toluene, as a consequence of cleaning the vials, was distilled by Dean Stark Distillation method. The volume of the distilled water was measured and the volume of the produced oil was calculated by subtraction. In addition to that, the remainder oil and toluene mixture was placed in a rotary evaporator to separate the produced oil. The separated oil was next placed in a desiccator, where its mass was measured twice a day for a few days until the mass changes were minimal.

The unpacked core samples were extracted by distillation, to measure the amount of oil and water left unproduced on the core. Toluene was used as the solvent. The duration of the core extraction process was three days for Oil A and one day for $n\text{-C}_{15}\text{H}_{32}$. The extracted dry core was then ignited at 600 °C for 16 hours to measure its weight loss as an indicator of its coke content. The same ignition process was repeated for a sample of the original un-saturated core to be used as a reference. Since the original core was a carbonate rock, it was not unusual that the reference sample exhibited a small amount of weight loss during ignition.

Depending on whether enough intact oil from centrifugation of the sample was available, viscosity and density measurements and simulated distillation analysis were performed on a sample of the produced oil, priority given to simulated distillation. Viscosity measurements were performed by a Brookfield viscometer (Model RVDV-1+) and densities were obtained by an Anton Paar density meter. Since the vaporization phenomenon in HPAI and its impact on the nature of the produced fraction of the oil and

consequently the fuel for combustion was of high interest in this study, a simulated distillation analysis was performed on produced oil samples of all tests.

3.7 Simulated Distillation

Samples of the original stock tank oil, produced oils from the air and nitrogen injection tests, as well as extracted oil from some post-test nitrogen injection cores were analyzed by simulated distillation to determine their single carbon number distribution, which would indicate the composition of the samples. The analysis of each sample was carried out with an Agilent 7890 Gas Chromatograph (GC) system equipped with an auto sampler. The HP Chemstation software controlled the operation of the GC, and the Sim. Dist. Expert 8.1 software was used to analyze the distillation results. The GC of the simulated distillation system has a 5 m long, 0.053 cm diameter capillary column. It elutes up to n-C₁₀₀ at 425 °C. The column temperature was raised at a reproducible rate and the area under the chromatogram was recorded throughout the analysis. Boiling points were assigned to the time axis from a calibration curve obtained under the same conditions from the retention time standard. Sim. Dist. Expert software was used to process the data obtained in the form of boiling point range distribution. Details of the method can be found in the ASTM D7169.

3.8 Test Design Strategy

Vaporization of the lighter fractions of the oil in an HPAI process is a major mechanism that not only acts as a drive mechanism but also affects the kinetics of the oxidation/combustion reactions in the sense of altering the type of available fuel for the reactions. Thus, as a primary stage it was inevitable to study the distillation behavior of the oil samples under the conditions of air injection tests. Also it was important to investigate the contribution of the sweeping effects of nitrogen from the injected air to the overall recovery of the process to understand the role of viscous drive and relative

permeabilities for further utilization in simulation models. Hence, in order to build the fundamental framework for this research, nitrogen injection tests at isothermal and ramped temperature conditions were designed to be conducted prior and also along with the air injection tests. A total of 15 tests were performed in the HPRT0 setup, 6 of which were nitrogen injection tests and the rest, air injection experiments. These experiments fell into the following categories:

1. *Ramped temperature, air injection experiments*: to study the kinetics of light oil oxidation with an emphasis to determine conditions where hydrocarbon vapor phase oxidation reactions are significant.
2. *Ramped temperature, nitrogen injection experiments*: to characterize the distillation behavior of the selected light oil when it is exposed to a heating ramp and distillation occurs in the absence of oxidation. This type of test also enables examination of the correlation between velocity of the evaporation front and interstitial gas.
3. *Isothermal, nitrogen injection experiment*: to determine the sweep efficiency of flue gas (nitrogen) drive at initial reservoir temperature conditions in the absence of thermal effects.

3.8.1 Operation Conditions

As was mentioned previously, the light oils selected for the HPRT0 experiments were a 37 °API paraffinic crude oil (Oil A) and a pure hydrocarbon ($n\text{-C}_{15}\text{H}_{32}$). The initial fluid saturations in the core varied as per the design of the tests. In a test that contained both oil and brine, on a mass basis, the average concentrations in the core samples were 89.3 % clean reservoir sand, 5.3 % oil, and 5.3 % synthetic brine. The core samples therefore had an initial gas saturation. In the tests where the cores were only saturated by oil or brine, the saturation of the absent fluid was given to the gas. For example, for a

test with no interstitial water, a mixture of 94.4% sand and 5.6% oil was packed, on a mass basis. The detailed initial saturations for all tests are tabulated in Table 3.2. While all tests were operated at 13.6 MPa, temperature conditions were different. Table 3.4 lists the operating conditions for each test in terms of pressure, gas injection flux, temperature history and initial saturations.

3.9 Sources of Error

Throughout the course of the experiments, proper care was taken to ensure the repeatability of the obtained data. The procedures mentioned in the previous sections were thoroughly followed during the porous media preparation, HPRT0 tests, and post-test core and fluids analysis. Although, every measure was taken to conduct a satisfactory test, heater controller and thermocouple malfunction in Tests 8 and 9 led to unsuccessful runs in terms of controlling and recording the temperature.

Design of the HPRT0 tests involves relatively small amounts of initial oil and water (10 g each on average) in the packed core mixture. Therefore one unavoidable error was in maintaining a solid material balance. Given the complex procedure of HPRT0 tests during production and post-test core and fluids analysis, dealing with very small amounts of water and volatile light oil samples was difficult. Modifications were done to the production system during the course of the experiments in order to minimize the error as was explained in section 3.5. However, other sources of error impacted the material balance inevitably. One was the loss of lighter ends (up to C_{10}) during extraction of water and oil from the post-test core.

Another source was the evaporation of water within the collector vessel during the time period between the completion of the test and the time it was possible to use the chemistry lab for the analysis.

For the air injection tests, the stoichiometric calculations for gas phase parameters were based on fuel and water of combustion. This is not very accurate since the gas compositions are dependent on the data obtained from the gas chromatograph. One source of error in GC readings was related to the early time when the helium (which was injected to pressurize the system) was being moved out of the reactor by the injected gas. Also during stoichiometric calculations of the oxidation/combustion reactions, it was assumed that all of the utilized oxygen had participated in bond scission reactions to generate water and carbon oxides. Lack of proper data and the inability to separate the amount of oxygen consumption between the bond scission and oxygen addition reactions led to inaccuracy in gas phase parameters.

Although the mass flow meter was calibrated for the HPRT0 tests, the readings of wet test meter installed on the outlet line did not agree with those of the mass flow meter. Fortunately this error was small and did not have a significant impact on the results. The fluxes reported in Table 3.4 are based on the mass flow meter setting whilst the calculations in this study were based on the wet test meter readings.

Table 3.4: Operational conditions for HPRT0 Tests; all pressures at 13.6 MPa

	Injected Gas	Injection Flux Based on Mass Flow Meter ($\text{sm}^3/\text{m}^2\text{h}$)	Injection Start Off Temperature ($^{\circ}\text{C}$)	Heating Rate ($^{\circ}\text{C}/\text{h}$)	HC Sample	Initial Oil Saturation (Wt %)	Initial Water Saturation (Wt %)
Test 1	Nitrogen	38.2	22	75	Oil A	5.31	5.37
Test 2	Air	38.2	22	60	Oil A	5.31	5.37
Test 3	Air	38.2	150	60	Oil A	5.31	5.37
Test 4	Air	38.2	180	40	Oil A	5.31	5.37
Test 5	Nitrogen	38.2	116	0	Oil A	5.31	5.37
Test 6	Air	12.7	150	60	Oil A	5.31	5.37
Test 7	Nitrogen	25.2*	22	60	Oil A	5.31	5.37
Test 8	Air	38.2	180	60	Oil A	5.31	5.37
Test 9	Air	38.2	180	60	Oil A	5.31	5.37
Test 10	Air	38.2	150	60	n-C ₁₅ H ₃₂	5.31	5.37
Test 11	Air	38.2	150	60	n-C ₁₅ H ₃₂	5.62	0
Test 12	Nitrogen	38.2	22	30	n-C ₁₅ H ₃₂	5.31	5.37
Test 13	Nitrogen	38.2	22	60	Oil A	5.62	0
Test 14	Nitrogen	38.2	60	75	None	0	5.67
Test 15	Air	12.7	150	60	Oil A	5.31	5.37

*Test 7 was designed to run at the same flux as Test 6; however, wet test measurement recordings during the test showed that the actual flow rate inside the reactor was higher. This was due to calibration of the mass flow meter.

Chapter Four: Experimental Results

In this chapter, the experimental results will be described. Fifteen air and nitrogen injection experiments were conducted on using a high pressure, 2000 psig (13.6 MPa), ramped temperature reactor. The gas injection fluxes were at either high ($38.2 \text{ sm}^3/\text{m}^2\text{h}$) or low ($12.6 \text{ sm}^3/\text{m}^2\text{h}$) levels. Two hydrocarbon samples were used in the study: light Oil A (37 °API) and pure $n\text{-C}_{15}\text{H}_{32}$. The operational conditions of the experimental runs including the type and flux of gas injection, hydrocarbon type, hydrocarbon and water saturation, and the rate of heating were previously summarized in Table 3-4.

The temperature history, liquid production history, and product gas composition plots for each test will be presented in this chapter along with a brief description. The liquid production curves show different number of data points due to the modifications made to the liquid collection system. A table is provided for each test, where the results of post-test core and fluid analysis are reported. More Details of the experimental data are presented in Appendices B, C and D.

4.1 Test 1: Ramped-Temperature Nitrogen Injection Test on Oil A

Since distillation or the vaporization-condensation of light components are the main mechanisms associated with the kinetics of air injection processes, Test 1 was designed to perform a preliminary study on characterizing the distillation and thermal cracking behavior of Light oils and Oil A in particular.

In Test 1 nitrogen was injected into the reactor while the whole reactor was heated from room temperature to $400 \text{ }^\circ\text{C}$ at a temperature ramp rate of $75 \text{ }^\circ\text{C/h}$. Figure 4-1 demonstrates the temperature profile, recorded by seven internal thermocouples, along with the liquid (oil plus water) production history for Test 1. An evaporation front formed

after 120 minutes of runtime (at 160 °C) that propagated through the core. The front's location was evident by a rapid reduction in temperature at the individual thermocouples due to the endothermic heat of vaporization. The first thermocouple (TC1) is located near the reactor inlet which contains dry coarse sand to prevent core material from entering the injection lines; therefore, it did not show an endothermic response as exhibited by the downstream thermocouples in the oil bearing portion of the core.

Figure 4-2 clearly highlights the extent of temperature drops at the thermocouples, using TC1 as the reference thermocouple. The drift in the baseline profile suggests a slight non-uniformity in the axial temperature, with the center portion of the core being at a higher temperature. This indicates axial heat losses at the inlet and outlet of the reactor. Since the entire reactor, according to the experimental procedure, was at a uniform temperature, vaporized hydrocarbon and water would not get a chance to condense inside the reactor until they exit through the outlet line and condensed in the liquid production trap. Condensation first occurred after the evaporation front had moved through the entire reactor length, being evident in Figure 4-1. The total oil recovery from the distillation/thermal cracking test was 74%. Also a total recovery of 74% was obtained for water.

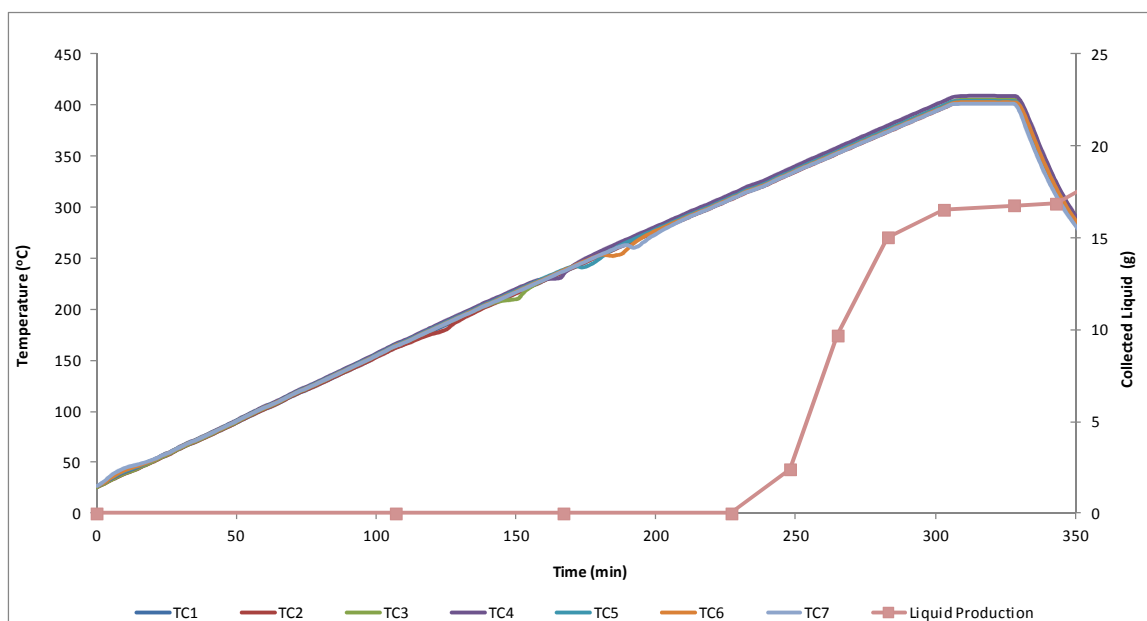


Figure 4-1: Temperature history, as recorded at the thermocouple (TC) locations in Test 1 (Oil A, nitrogen, $38.2 \text{ sm}^3/\text{m}^2\text{h}$), and liquid production (oil + water)

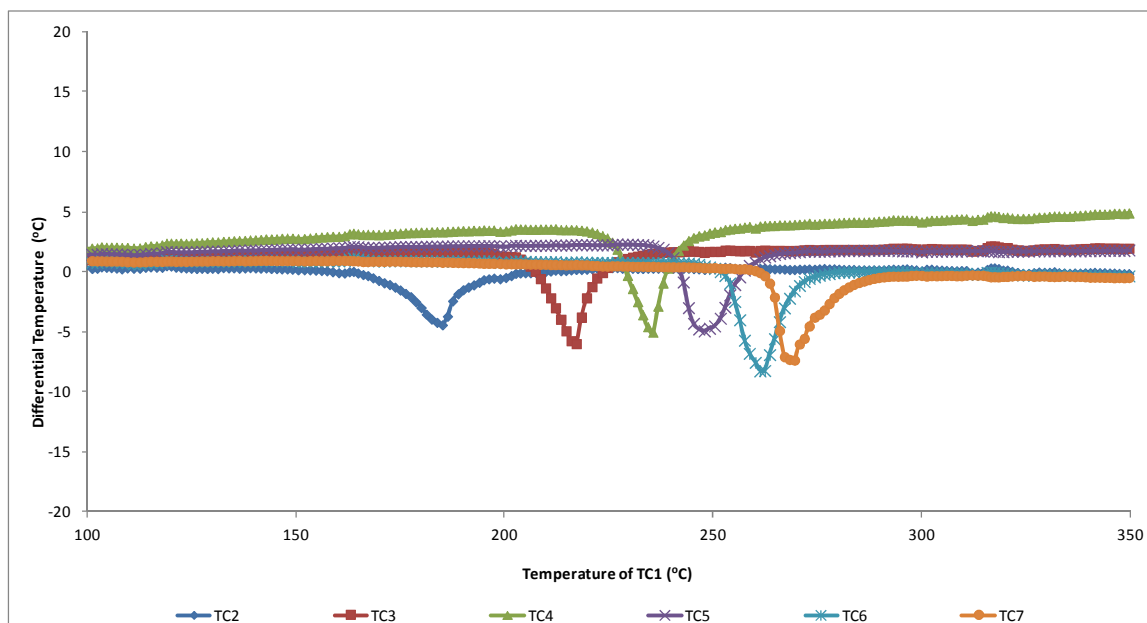


Figure 4-2: Differential temperature with reference to TC1 as the evaporation front moves through thermocouple (TC) locations in Test 1 (Oil A, nitrogen, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

The endothermic evaporation front caused an average of 7 °C temperature reduction at the thermocouple locations while traversing the entire core. Obviously the extent of the temperature drop depended on the heat capacities of the rock and fluids, since the thermocouples 1-7 are located in the center of the core. Meanwhile, the heaters maintained a minimal temperature change at the four thermocouples located on the wall of the reactor.

Table 4-1: Summary of post test core and fluid analysis for Test 1

Recovery Analysis		Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>		13.75	13.91
<i>Mass of Produced Liquid (g)</i>		10.24	10.33
<i>Recovery (%)</i>		74.47	74.26
Mass of Residual Liquid from Core Extraction (g)		Oil	Water
		0.99	0.30
Mass of Residual Solid (Coke) from Core Ignition (g)		0.20	
Material Balance Error (%)		Oil	Water
		16.87	23.58
Post Test Liquid Analysis			
<i>Density of Produced Oil (g/cm³)</i>		0.84	
<i>PH of Produced Water</i>		4.88	

Table 4-1 presents a summary of the post test core and fluid analysis. The results of SARA fraction analysis and simulated distillation can be found in the Appendices A and B. As was mentioned earlier, the material balances for early tests were not satisfactory. However, this problem was later resolved (Test 7 onward) with a modified design for the liquid traps and the material balance error was minimized.

4.2 Test 2 and Test 3: Ramped-Temperature Air Injection Tests on Oil A

The first two air injection experiments that were performed to simulate the HPAI process under ramped temperature conditions are reported in this section. While the air injection fluxes for these two tests were identical, the temperature at which injection of air commenced, was treated as a variable parameter to study its effect on oxidation kinetics. Details of the operating conditions were provided in Table 3-4.

In Test 2, air injection commenced at room temperature and was continued while the core temperature was being ramped at a rate of 60 °C/h. As can be observed from the temperature profile (Figure 4-3), an exothermic reaction zone formed at 180 °C and while advancing through the thermocouple locations 2 to 7, it resulted in an average rise of 50 °C in the temperature measured at these thermocouples. However, Zone 6 showed a narrower peak associated with a higher temperature indicating a greater reaction rate than was observed at the other thermocouple locations. The liquid production history (Figure 4-3) shows almost an immediate response after the reaction zone is observed to form. This immediate response during the air injection test directs emphasis on the displacing effects of the reaction front when being compared to delayed production in the nitrogen test (Test1) which occurred after the evaporation front had moved through the entire core. Total oil recovery for this test was 62% as reported in the following table.

Table 4-2: Summary of post test core and fluid analysis for Test 2

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	13.73	13.88
<i>Mass of Produced Liquid (g)</i>	8.60	9.25
<i>Recovery (%)</i>	62.65	66.64
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.04	0.30
Mass of Residual Solid (Coke) from Core Ignition (g)	0.08	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	5.01	3.11
Mass of Apparent Water of Combustion (g)	by material balance	by stoichiometry
	-4.33	13.24

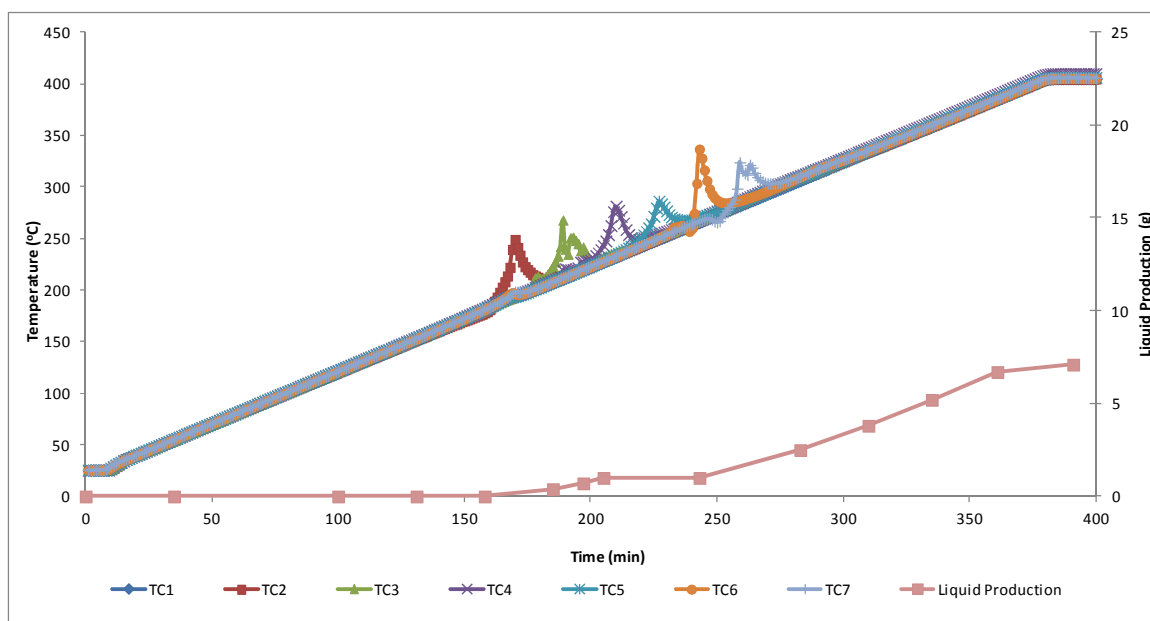


Figure 4-3: Temperature history, as recorded at the thermocouple (TC) locations in Test 2 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$), and cumulative liquid production (oil + water)

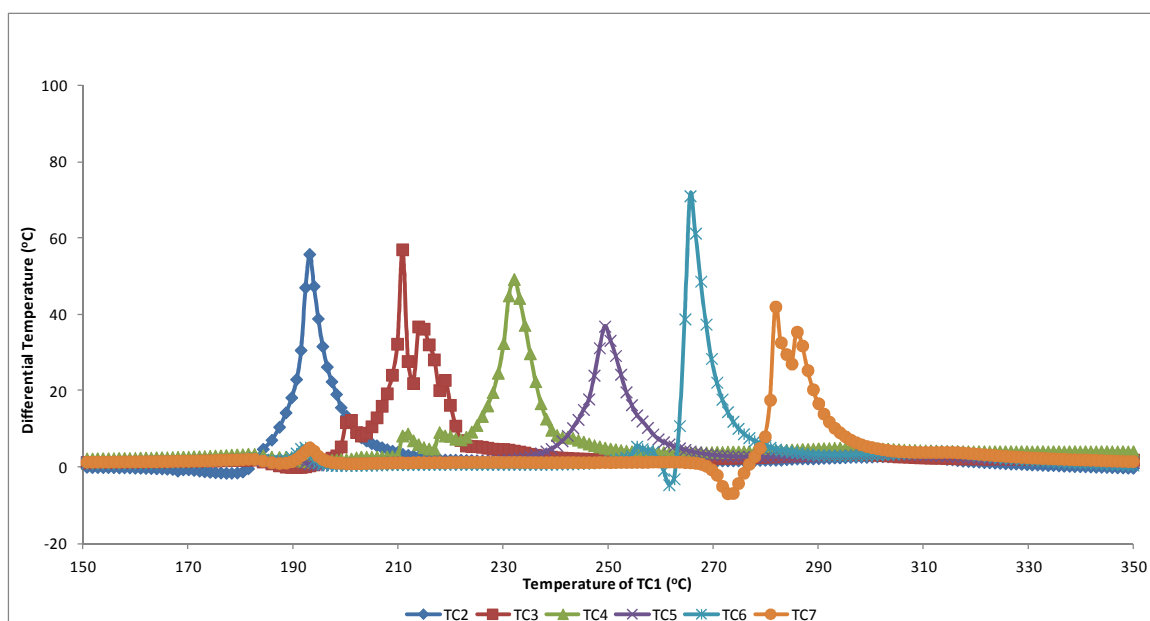


Figure 4-4: Differential temperature with reference to TC1 as the evaporation front moves through thermocouple (TC) locations in Test 2 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

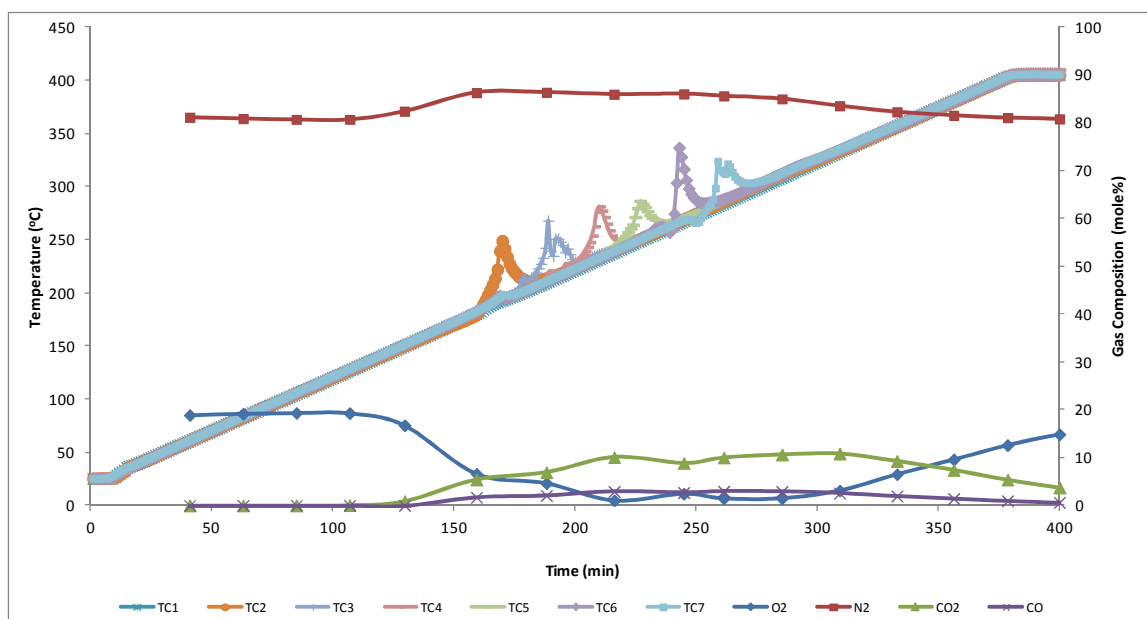


Figure 4-5: Product gas composition and temperature history for air injection Test 2 (Oil A, air, 38.2 sm³/m²h)

The product gas composition as observed for Test 2 is shown in Figure 4-5 with reference to the temperature history. Since there was a delay between the times that the gas was generated inside the reactor and when it was sampled by the gas chromatograph (GC), this delay was calculated based on temperature, pressure, location of the reaction zone inside the reactor, and geometry of the HPRT0 set-up. Therefore, the gas compositions are plotted against the corrected time that they were produced inside the reactor.

Essentially complete oxygen uptake was achieved during the period that the reaction front propagated through the core. Nitrogen concentration increased in response to the formation of the reaction zone, then tended to decrease over the duration of the test. High nitrogen concentrations indicate either consumption of hydrogen and oxygen to form liquid water or the removal of oxygen from the gas phase due to oxygen addition reactions.

Test 3 was performed under the same conditions as Test 2 with the exception that in Test 3 the core was preheated to 150 °C prior to air injection. Preheating of the core was intentionally performed to examine the effect that the temperature at onset of air injection has on the temperature at which the vapor phase burn initiates. The higher temperature for onset of air injection was expected to reduce the immobilization effects of oxygen addition reactions as the core is heated from room temperature to 150 °C. According to the temperature profile (Figure 4-6), the temperature for onset of the propagating reaction zone appeared to be slightly higher than was observed during Test 2. This reflects the certain amount of time (ignition delay) needed for generation of compounds by oxygen addition and oxygen induced cracking reactions. The average temperature rise observed at thermocouple locations due to exothermic reactions was approximately the same as for Test 2. Since the air injection rate in both tests was the same, according to the rule of thumb heat of reaction of 3716 kJ/sm³ of air it was expected that the two tests would exhibit similar global heat generation and consequently temperature rise. Similar to Test 2, a higher temperature rise was observed at Zone 6.

Figures 4-6 and 4-7 demonstrate that, both thermocouple locations 6 and 7 exhibited distinct endothermic dips just prior to development of the exothermic reaction zones. The endothermic temperature dips observed at Zones 6 and 7 suggest that the vaporization front velocity increased with temperature and was no longer masked by the exothermic reaction front. Similar behavior can be seen in Figures 4-3 and 4-4 (Test 2). The higher total production for Test 3 over that of Test 2 is a reflection of the longer period of low temperature exposure to oxygen and thus, higher extent of oxygen addition reactions experienced during Test 2.

The product gas composition profiles for Test 3 are shown in Figure 4-8 with reference to the temperature history. As was observed during Test 2, the nitrogen concentration

showed a high level when the reaction zone was formed and then decreased as the test proceeded. High oxygen utilizations were observed as the reaction front propagated but the slow rise in oxygen and slow decline in carbon dioxide concentration at the end of the test indicates the presence of a solid residual fuel after the reaction front has passed through the core. The long time and low energy generation observed as the residual was consumed indicates a slow reaction rate for the solid coke-like residue.

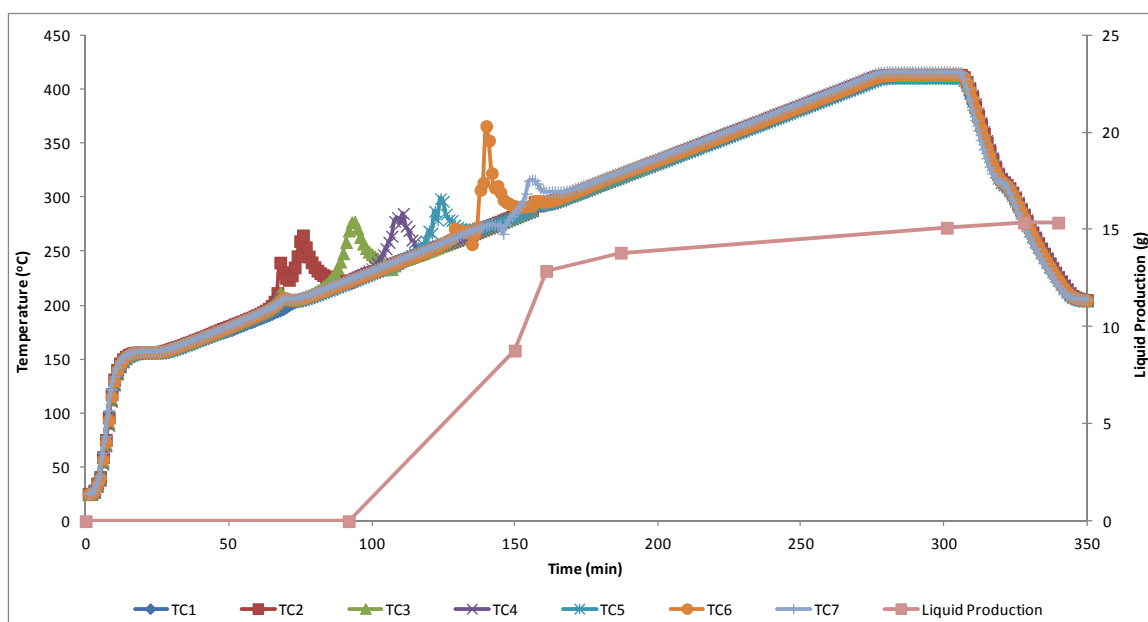


Figure 4-6: Temperature history, as recorded at the thermocouple (TC) locations in Test 3 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$), and cumulative liquid production (oil + water)

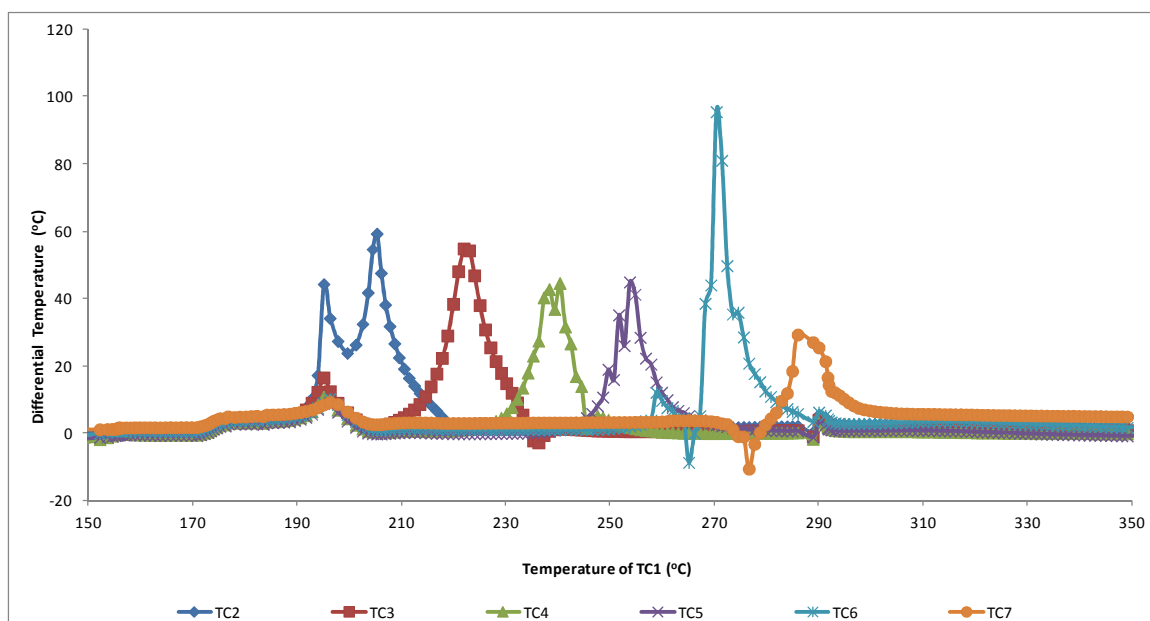


Figure 4-7: Differential temperature with reference to TC1 as the evaporation front moves through thermocouple (TC) locations in Test 3 (Oil A, air, 38.2 sm³/m²h)

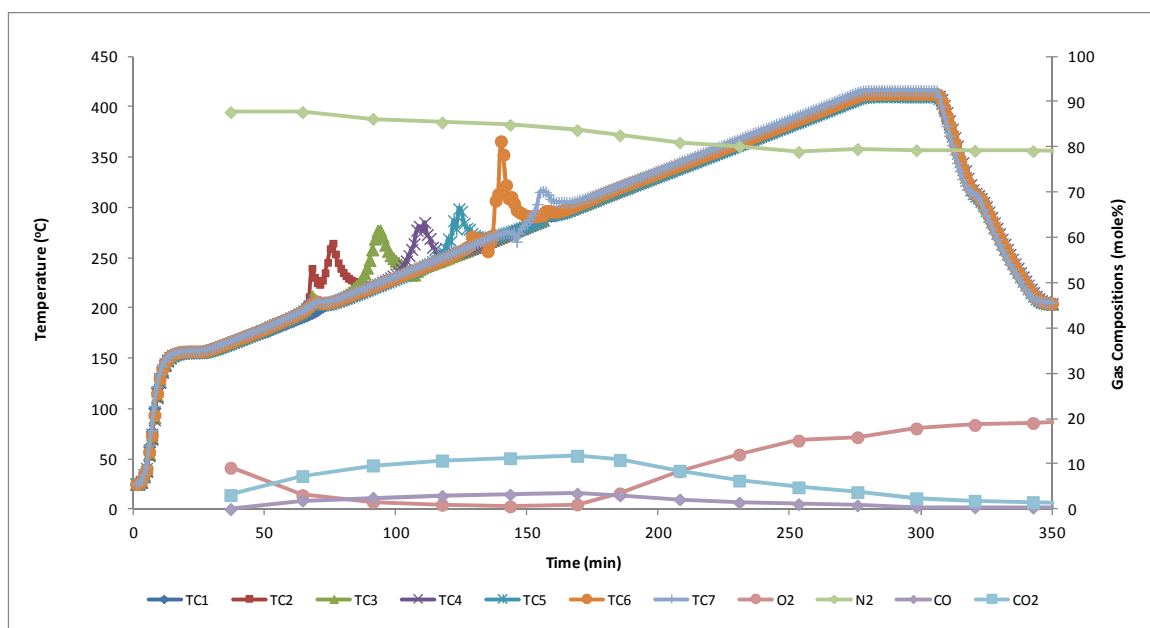


Figure 4-8: Product gas composition and temperature history for air injection Test 3 (Oil A, air, 38.2 sm³/m²h)

Table 4-3: Summary of post test core and fluid analysis for Test 3

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	14.59	14.75
<i>Mass of Produced Liquid (g)</i>	10.73	12.90
<i>Recovery (%)</i>	73.56	87.45
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.18	0.00
Mass of Residual Solid (Coke) from Core Ignition (g)	0.09	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	3.59	4.83
Mass of Apparent Water of Combustion (g)	by material balance	by stoichiometry
	-1.85	7.96

4.3 Test 4, Test 8, and Test 9: Ramped-Temperature Air Injection Tests on Oil A

In Test 4 the core was preheated up to 180 °C, which is 30 °C higher than the preheating temperature of Test 3. This test was intended to further study the effect of preheating and the consequent limitation of oxygen addition reactions at lower temperatures. A temperature ramp rate of 40 °C/h was scheduled for Test 4. According to the temperature profile of Test 4 (Figure 4-9), the onset temperature for formation of the first reaction zone was 200 °C, which according to the ramp rate of 40 °C/h implies a 35 minute of ignition delay for Test 4 which is identical to that of Test 3. The oil recovery in Test 4 was slightly lower and the average temperature rise in the reaction zones was

slightly higher than that observed in Test 3. This indicates a slightly different kinetic path in Test 4, due to a different heating rate and preheating temperature. Oxidation reactions occurring in a narrower zone were evident by the rapid temperature rise in TC6 as can be observed in the temperature profile, Figure 4-9.

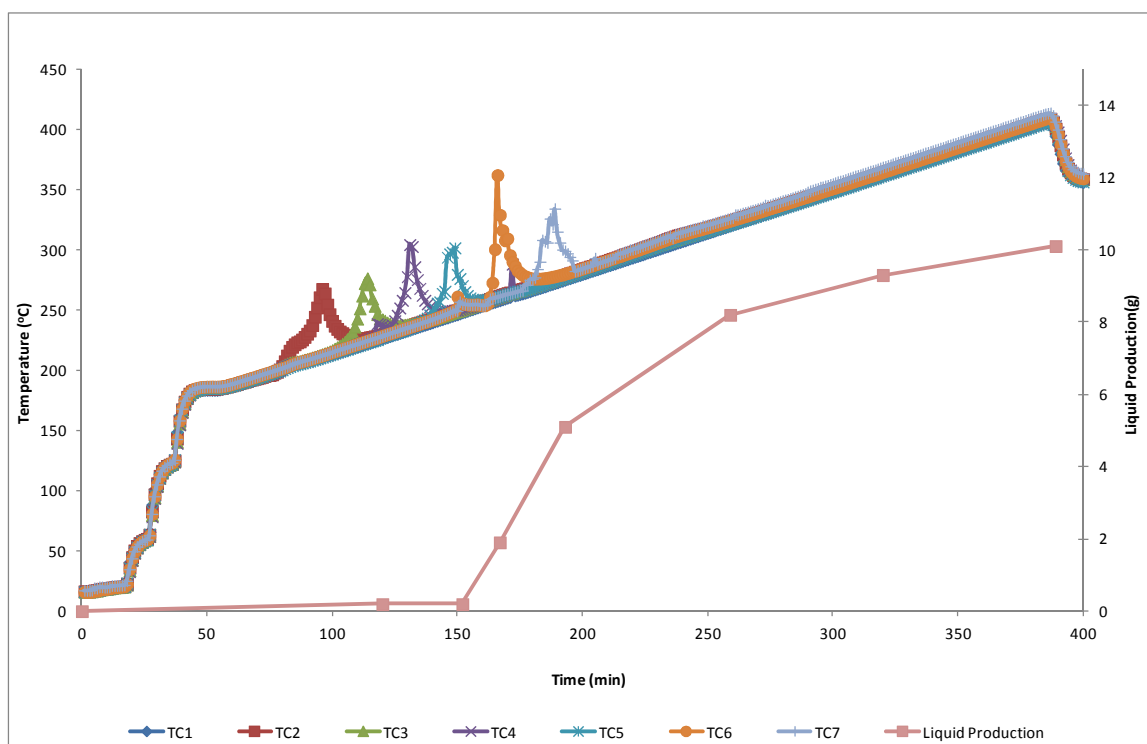


Figure 4-9: Temperature history, as recorded at the thermocouple (TC) locations in Test 4 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$, $40 \text{ }^\circ\text{C/h}$), and cumulative liquid production (oil + water)

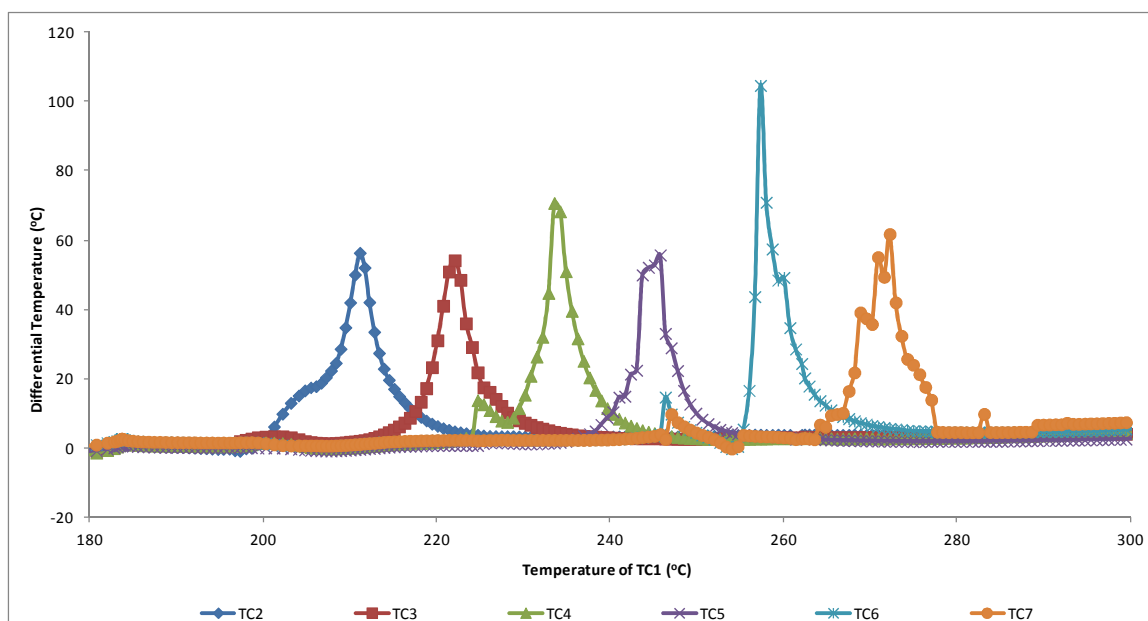


Figure 4-10: Differential temperature with reference to TC1 as the evaporation front moves through thermocouple (TC) locations in Test 4 (Oil A, air, 38.2 $\text{sm}^3/\text{m}^2\text{h}$, 40 $^\circ\text{C}/\text{h}$)

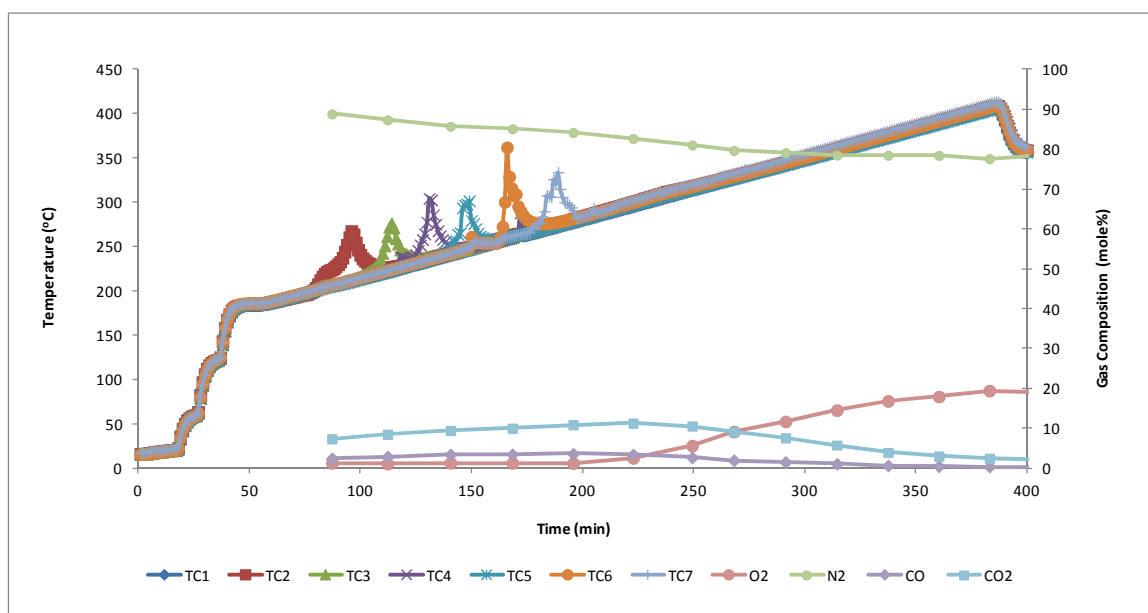


Figure 4-11: Product gas composition and temperature history for air injection Test 4 (Oil A, air, 38.2 $\text{sm}^3/\text{m}^2\text{h}$, 40 $^\circ\text{C}/\text{h}$)

Table 4-4: Summary of post test core and fluid analysis for Test 4

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	14.34	14.50
<i>Mass of Produced Liquid (g)</i>	7.53	9.00
<i>Recovery (%)</i>	52.50	62.05
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.16	0.00
Mass of Residual Solid (Coke) from Core Ignition (g)	0.10	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	6.55	8.01
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	-5.50	8.96

Since Test 4 was performed at a heating rate of 40 °C/h, in order to be able to compare the kinetics of this Test to Test 3, attempts were made to repeat Test 4 with a heating rate of 60 °C/h (identical to that of Test 2 and Test 3). Test 8 was designed for this purpose. However, unfortunately due to heaters' malfunction, the temperature profile for Test 8 could not be captured. Nevertheless, the production data for Test 8 are reported in this chapter. Since Test 8 was not successful in its purpose, it was repeated as Test 9. Although in Test 9 a desired stable heating rate could be established during the propagation of the reaction zone, in the preheating phase of this test the heaters failed to operate according to the computer defined schedule. The unfavorable results of this

event can be observed in the temperature profile of Test 9 (Figure 4-12) as the temperature increases up to 300 °C for the first 100 minutes of runtime. This was caused by malfunction of the Heater 4 and also the 6th internal thermocouple (TC6) which is evident in Figure 4-12. There's almost a 10 °C temperature difference along the reactor as a result of the same problem. In Figure 4-12 also is plotted the cumulative weight of the produced liquids as was measured by a digital weight scale and logged by the computer in Test 9. The weight increased relative to the temperature ramp indicating the impact of thermal stress on the scale and thus it's deficiency in accurate measurement of the weight.

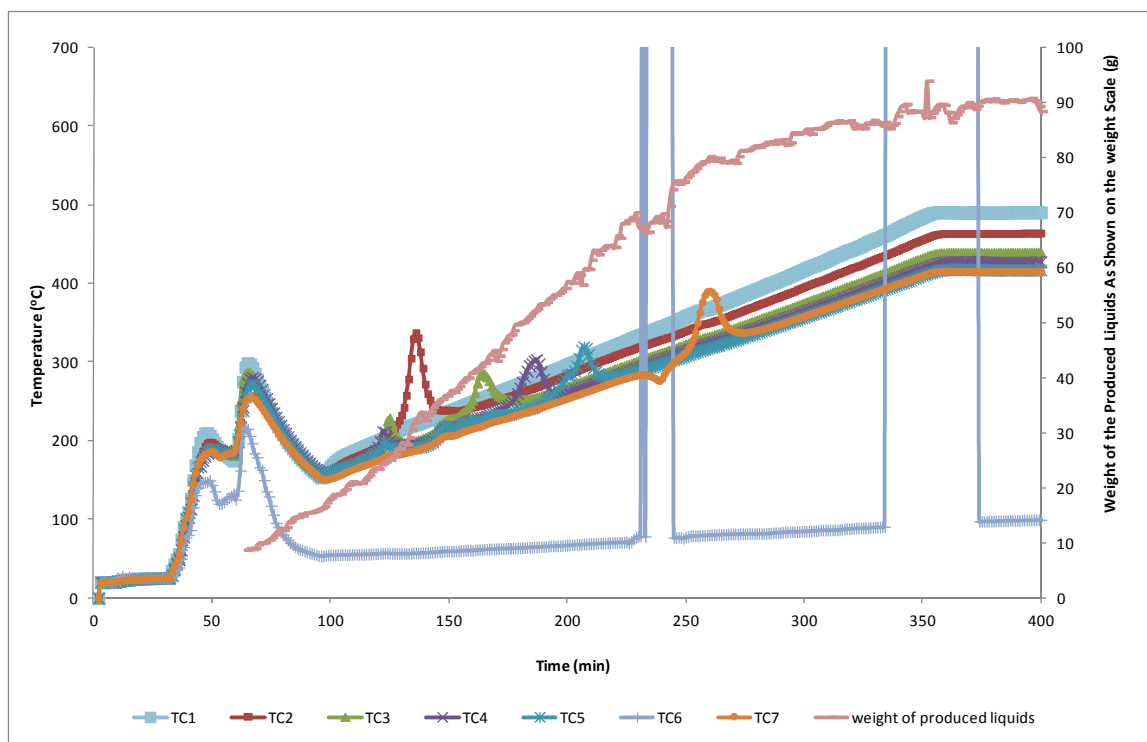


Figure 4-12: Temperature history, as recorded at the thermocouple (TC) locations in Test 9 (Oil A, air, 38.2 sm³/m²h), and liquid production (oil + water) as shown by weight scale

Table 4-5 : Summary of post test core and fluid analysis for Test 8

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	13.13	13.43
<i>Mass of Produced Liquid (g)</i>	5.91	14.50
<i>Recovery (%)</i>	45.02	108.00
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	3.01	0.42
Mass of Residual Solid (Coke) from Core Ignition (g)	0.00	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	4.21	1.72
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	1.49	6.30
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.8272 at 25 °C, 0.8163 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	3.03 at 25 °C, 2.02 at 40 °C	
<i>PH of Produced Water</i>	6.81	

Table 4-6: Summary of post test core and fluid analysis for Test 9

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	13.23	13.52
<i>Mass of Produced Liquid (g)</i>	6.05	19.85
<i>Recovery (%)</i>	45.75	146.77
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.02	0.37
Mass of Residual Solid (Coke) from Core Ignition (g)	0.00	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	7.16	4.58
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	6.70	6.56
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.8337 at 25 °C, 0.8223 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	3.20 at 25 °C, 2.12 at 40 °C	

Although the amount of apparent water of combustion for both Tests 8 and 9 are very similar, the amount calculated from the material balance for Test 9 is much closer to the predicted value by stoichiometric calculations. This is indicative of lower extents of the oxygen addition reactions in Test 9, where higher temperature conditions, due to operational problems were present during the test.

4.4 Test 5: Isothermal Nitrogen Injection on Oil A

The thermal effect of the combustion front, as a drive mechanism, has been often neglected in the modeling of the HPAI process and HPAI has been treated as a flue gas derived recovery process. Test 5 was intended to compare the recoveries under the two conditions of sole flue gas drive and presence of thermal drive.

In Test 5, Nitrogen was injected at reservoir temperature in order to simulate the recovery mechanism of flue gas injection at reservoir conditions. A distinct evaporation front formed during the test which traveled through thermocouple locations 2-7 (Figure 4-13). The test was shut down before the evaporation front could cause the last endothermic dip at thermocouple 7.

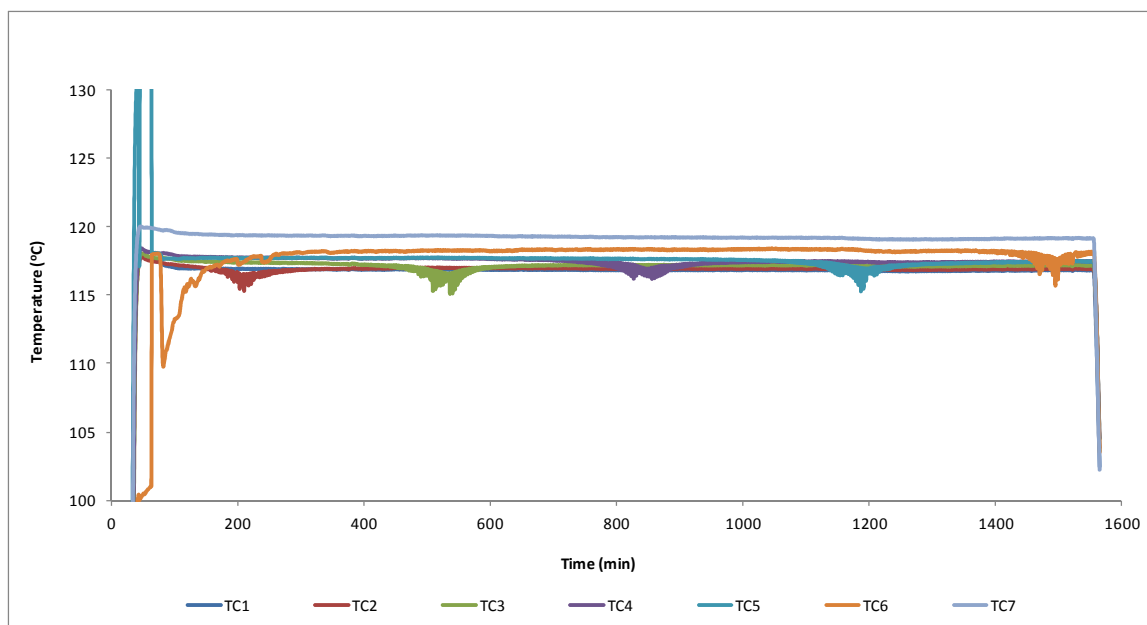


Figure 4-13: Temperature history, as recorded at thermocouple (TC) locations in Test 5 (Oil A, isothermal nitrogen, 38.2 sm³/m²h)

Table 4-7 Summary of post test core and fluid analysis for Test 5

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	15.66	13.65
<i>Mass of Produced Liquid (g)</i>	2.88	2.30
<i>Recovery (%)</i>	18.39	16.86
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	5.34	0.10
Mass of Residual Solid (Coke) from Core Ignition (g)	0.28	
Material Balance Error (%)	Oil	Water
	45.74	82.41

The total oil recovery for Test 5 was 18%, which reflects the contribution of flue gas drive at reservoir temperature and pressure conditions. However, if this number is compared to the 74% recovery of the oil in the air injection test (Test 3), it emphasizes the significant contribution of the thermal front effects to the incremental oil recovery.

4.5 Test 6 and Test 15: Ramped-Temperature Air Injection Tests on Oil A at Low Flux

So far all the reported tests were conducted at a high level of injection flux. In order to determine the effect of reduced injection flux on these types of tests, Test 6 was performed on Oil A at a flux of $12.7 \text{ sm}^3/\text{m}^2$. Air injection started at 150°C and continued while the core temperature was being ramped at a rate of $60^\circ\text{C}/\text{h}$. Figure 4-14 shows the temperature profile, along with the liquid production for Test 6. The last data point on the liquid production curve corresponds to the time of 300 minute. The duration of Test 6 was 1407 minutes; however for the sake of the clarity of the curves in Figure 4-14 the temperature history is shown for the first 300 minutes where the main vaporization and oxidation/combustion events were dominant. Final liquid production for Test 6 was 15.6 g as reported in Table 4-7.

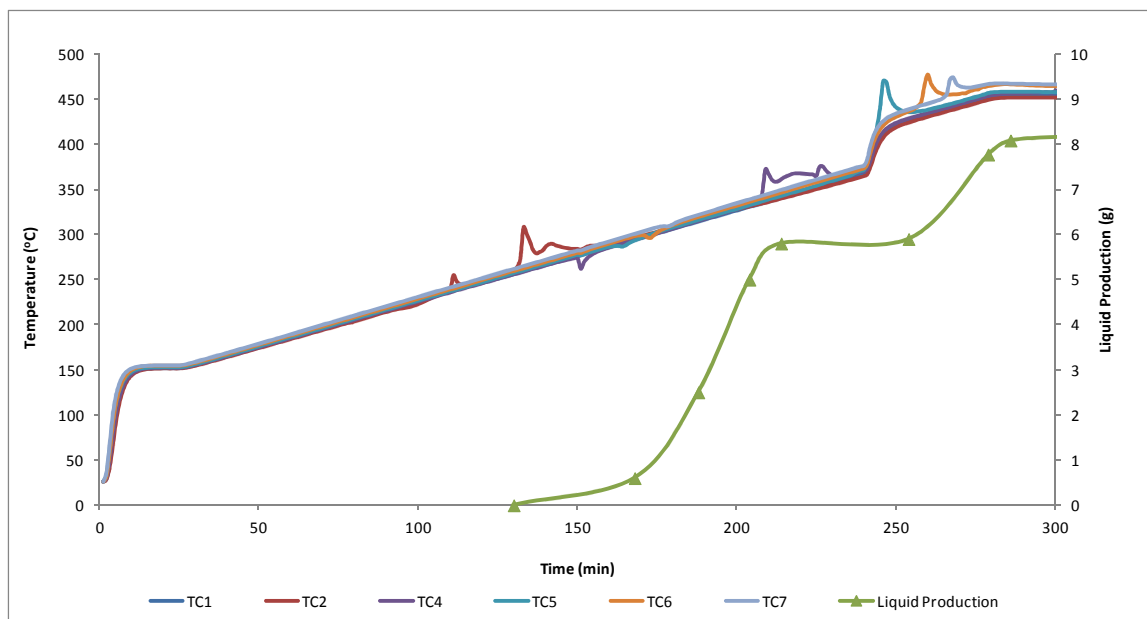


Figure 4-14: Temperature history and liquid production for Test 6 (Oil A, air, $12.75 \text{ sm}^3/\text{m}^2\text{h}$)

An evaporation front formed at 215 °C and propagated through the core followed by an oxidation/combustion front which formed at 235 °C. It is noted that during Test 6, the third thermocouple (TC3) failed on pressure-up and also the rapid jump in the system temperature at 370 °C was due to a problem with the heater control algorithm.

Figure 4-15 presents the temperature difference between TC1 and the downstream thermocouples for Test 6. Propagation of the evaporation front ahead of the oxidation/combustion front is highlighted in this figure.

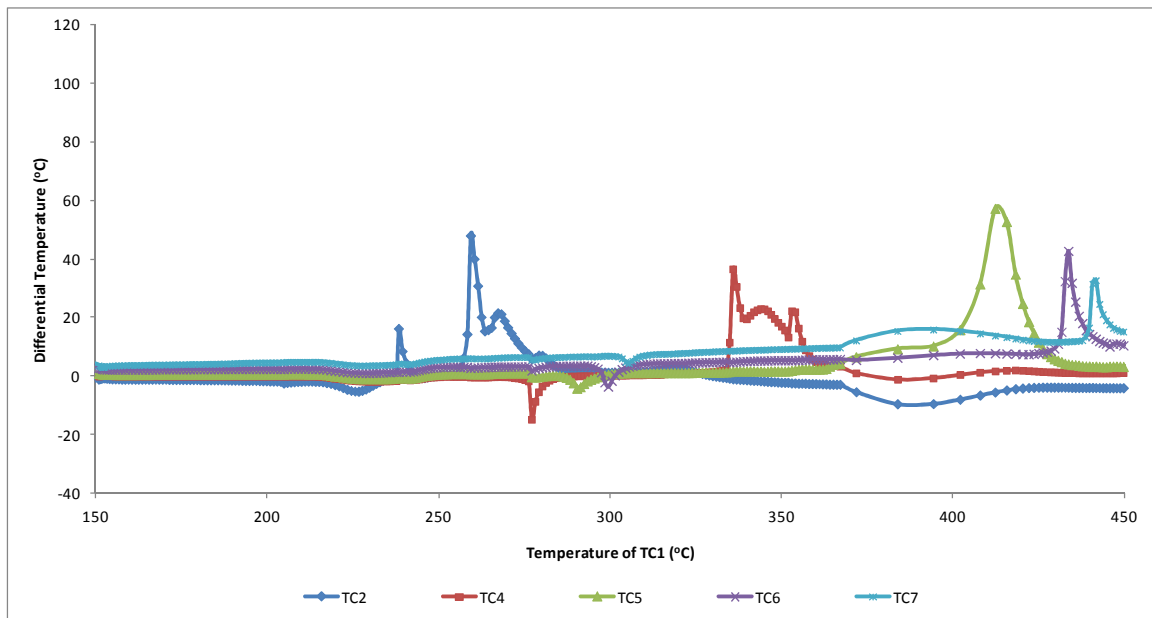


Figure 4-15: Differential temperature with reference to the first thermocouple (TC1) for Test 6 (Oil A, air, 12.75 sm³/m²h)

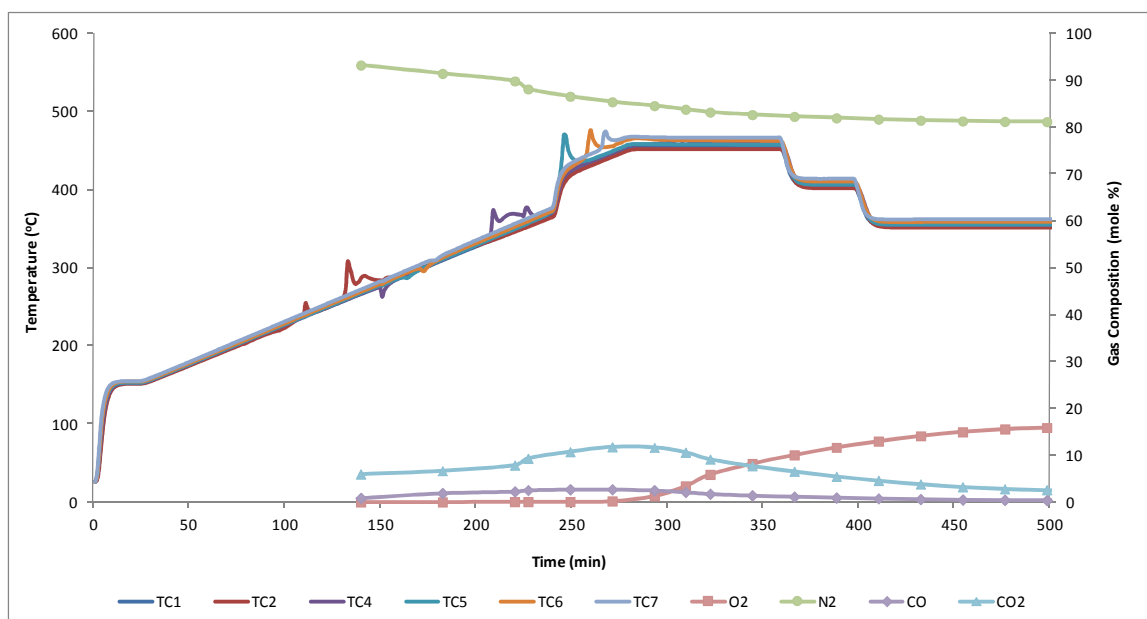


Figure 4-16: Temperature history and product gas composition for Test 6 (Oil A, air, 12.75 sm³/m²h)

Total oil recovery for Test 6 was 50% which is 25% less than that of the 38.12 sm³/m²h air injection Test 3, performed on Oil A under the same pressure and heating ramp conditions. This reflects the longer time period and higher temperature at which the exothermic front developed causing the residual hydrocarbon to experience a greater degree of oxygen addition reactions, hence the lower oil recovery. Very slow build up of the oxygen concentration in the product gas, as shown in Figure 4-16, indicates the slow consumption of a solid residue left on the core by oxygen addition reactions. This behavior emphasizes that “coke” is a very slowly reacting material and questions the traditional assumption of coke as the main fuel for oxidation/combustion reactions in light oils.

Table 4-8: Summary of post test core and fluid analysis for Test 6

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	15.56	13.56
<i>Mass of Produced Liquid (g)</i>	7.75	7.85
<i>Recovery (%)</i>	49.79	57.90
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.06	0.19
Mass of Residual Solid (Coke) from Core Ignition (g)	0.08	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	7.68	2.14
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	-5.52	4.16

The sudden rise in system temperature at minute 230 in Test 6, which was caused by the heater control algorithm as stated before, possibly changed the path of the kinetics for the combustion reactions. Therefore, it was decided to repeat this run in Test 15. Test 15 was conducted under identical operational conditions to Test 6. Figure 4-17 presents the temperature history along with the cumulative liquid production which was measured through a new procedure for liquid collection. As was explained in Section 3.5 in Chapter 3 the new collection system consisted of four containers that could collect the liquid production during four selected consecutive time periods. Like Test 6, the final

amount of production cannot be observed on the plot, due to the long duration of the test. 17.8 grams of total oil and water were produced in Test 15 as reported in Table 4-9.

Unlike the high flux tests, where the reaction zone advances through the thermocouple locations with a fairly constant rate, the velocity of the propagation of the oxidation/combustion front increases with temperature in Test 15 (and Test 6) as can be observed in Figure 4-17. The velocity of a vaporization or combustion front will be discussed in detail in Chapter 5.

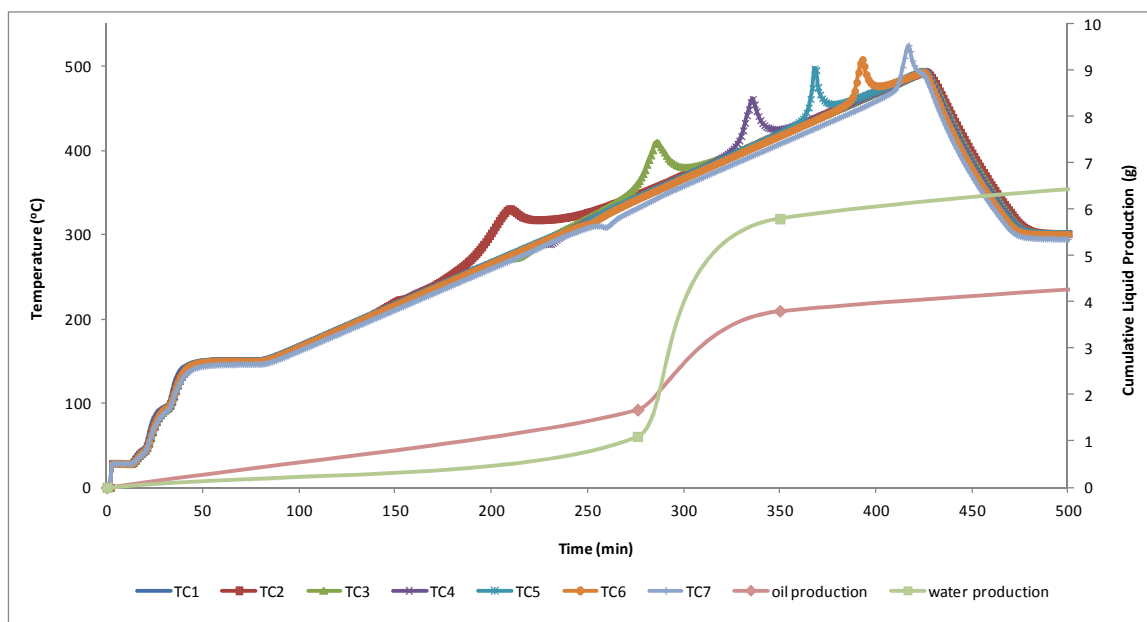


Figure 4-17: Temperature history and liquid production for Test 15 (Oil A, air, 12.75 sm³/m²h)

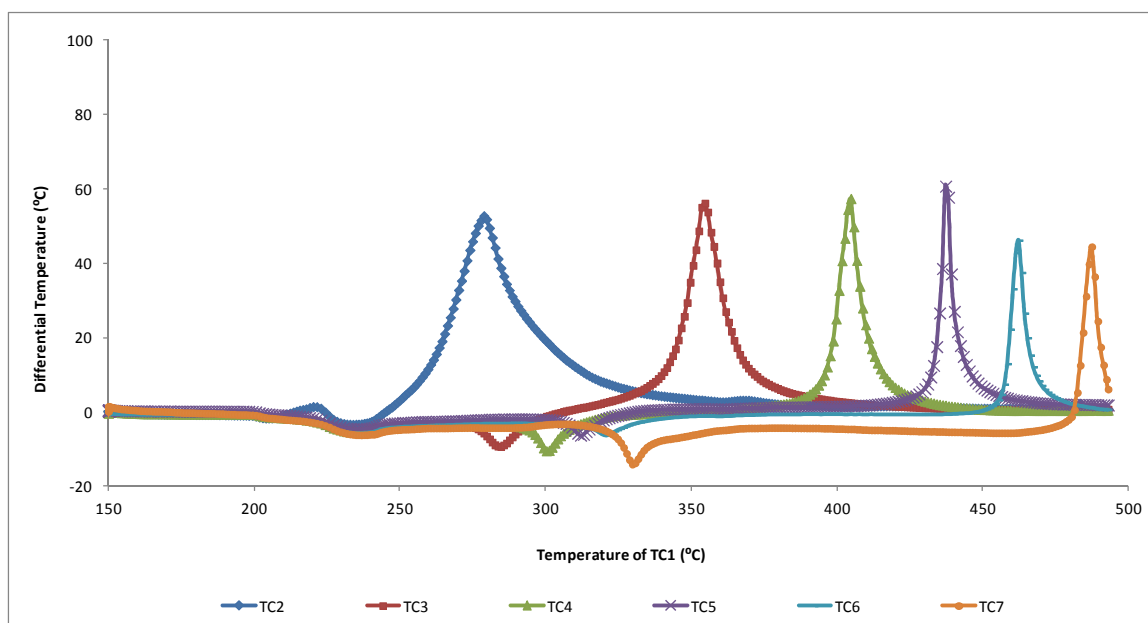


Figure 4-18: Differential temperature with reference to the first thermocouple (TC1) for Test 15 (Oil A, air, 12.75 sm³/m²h)

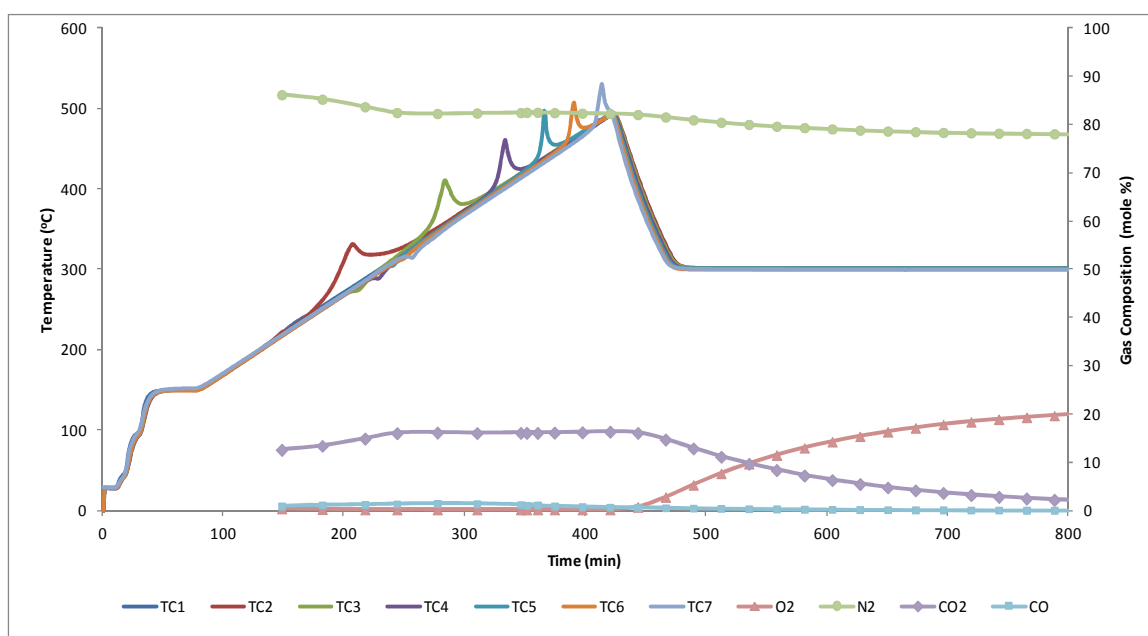


Figure 4-19: Temperature history and product gas composition for Test 15 (Oil A, air, 12.75 sm³/m²h)

Table 4-9: Summary of post test core and fluid analysis for Test 15

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	10.16	10.16
<i>Mass of Produced Liquid (g)</i>	6.34	11.50
<i>Recovery (%)</i>	62.37	113.13
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.02	0.10
Mass of Residual Solid (Coke) from Core Ignition (g)	0.96	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	3.82	4.58
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	1.24	8.96
Post Test Liquid Analysis		
<i>PH of Produced Water</i>	2.77	

4.6 Test 7: Ramped-Temperature Nitrogen Injection Test on Oil A at Low Flux

In order to highlight the distillation characteristics of Oil A under the low injection flux, Test 7 was performed under the same conditions as Test 6, with the exception that nitrogen was injected into the core instead of air. An evaporation front formed at 210 °C (Figure 4-20). This is identical to the temperature at which an evaporation front formed in Test 6. The evaporation front propagated through the core in a similar fashion to the evaporation front in Test 6.

In the high flux nitrogen injection test on Oil A (Test 1), the evaporation front formed at 160 °C. In Tests 6 and 7, formation of the evaporation front at 210 °C, suggests that phase behavior of the mixture is considerably affected by the nitrogen injection flux.

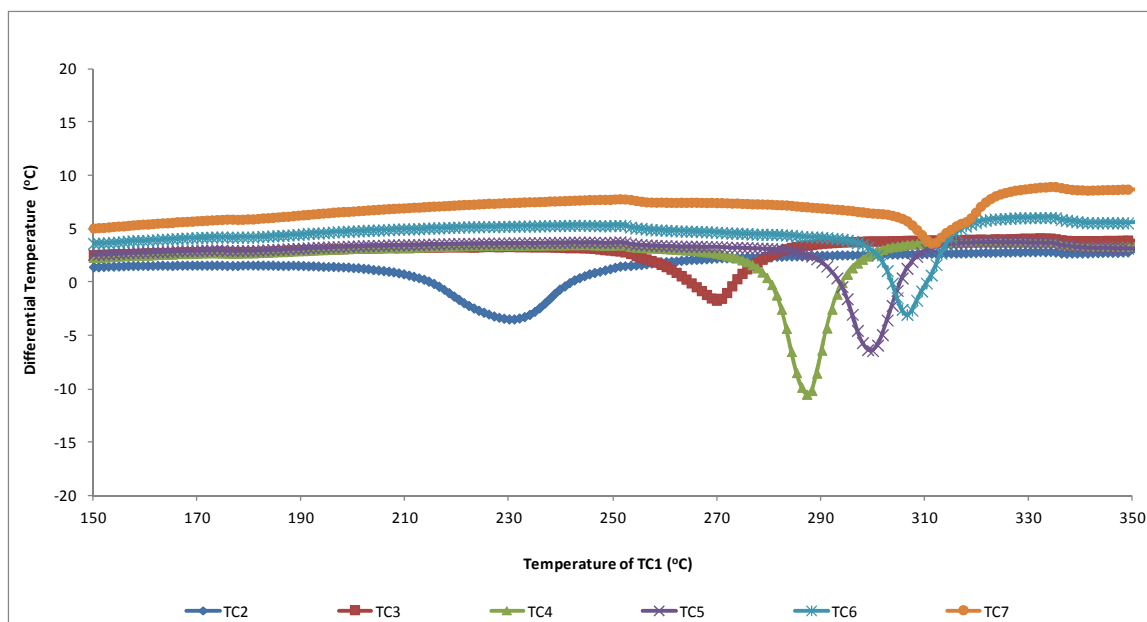


Figure 4-20: Differential temperature with reference to the first thermocouple (TC1) for Test 7 (Oil A, nitrogen, 12.75 sm³/m²h)

Table 4-10: Summary of post test core and fluid analysis for Test 7

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	14.85	15.19
<i>Mass of Produced Liquid (g)</i>	8.85	13.72
<i>Recovery (%)</i>	59.59	90.34
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	5.35	0.85
Mass of Residual Solid (Coke) from Core Ignition (g)	1.61	
Material Balance Error (%)	Oil	Water
	-6.43	4.06
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.8270 at 25 °C, 0.8162 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	2.82 at 25 °C, 1.95 at 40 °C	
<i>PH of Produced Water</i>	5.96	

4.7 Test 10: Ramped-Temperature Air Injection Test on n-C₁₅H₃₂

The pure hydrocarbon, normal Pentadecane (n-C₁₅H₃₂), has the highest concentration among the hydrocarbon components of Oil A according to the single carbon number distribution of Oil A (Figure 3-5). Based on this, n-C₁₅H₃₂ was considered for Tests 10 (and also for Tests 11, and 12 which will be discussed in the upcoming sections) as a pure hydrocarbon component that can represent similar characteristics to Oil A.

In Test 10, which is a high flux air injection test, the core was preheated up to 150 °C prior to air injection. The temperature profiles for Test 10 are shown in Figure 4-21 along with the product gas composition. A combustion front formed at 175 °C. While propagating through thermocouple locations 2-7 the average temperature rise was 53.5 °C (Figure 4-22). This number is very close to that of Test 3 (54.6 °C) which was a high flux air injection on Oil A. Since HPRT0 tests are oxygen-limited, according to the rule of thumb heat of reaction of 3716 kJ/sm³ (100 BTU/SCF) of air, it is expected that both Oil A and n-C₁₅H₃₂ would exhibit similar heat generation and consequently temperature rise.

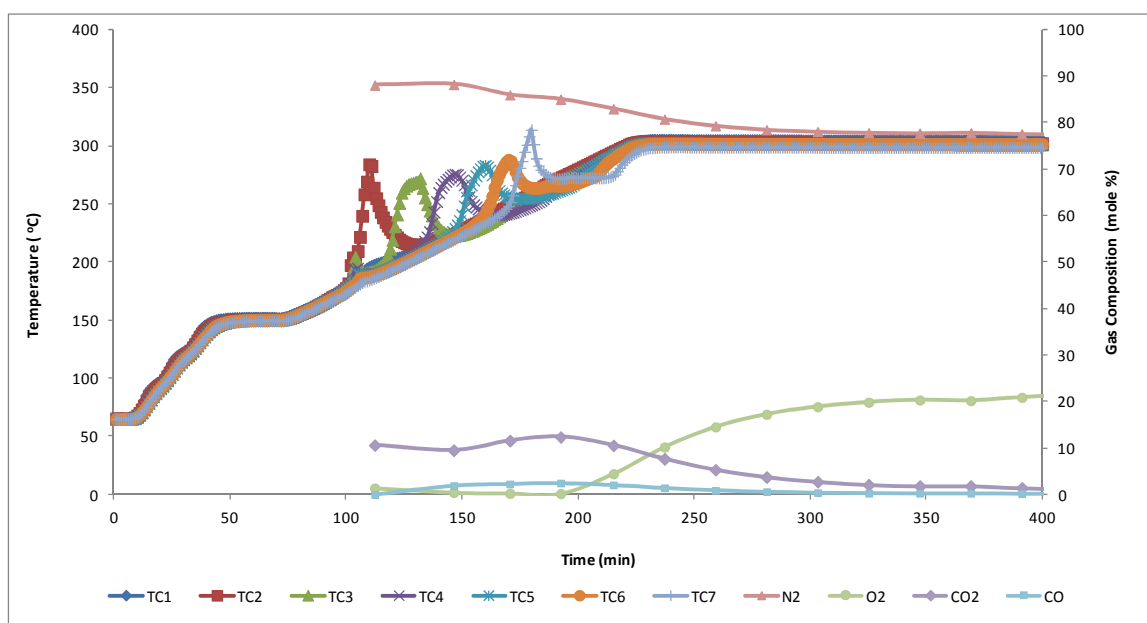


Figure 4-21: Temperature history and product gas composition for Test 10 (n-C₁₅H₃₂, air, 38.2 sm³/m²h)

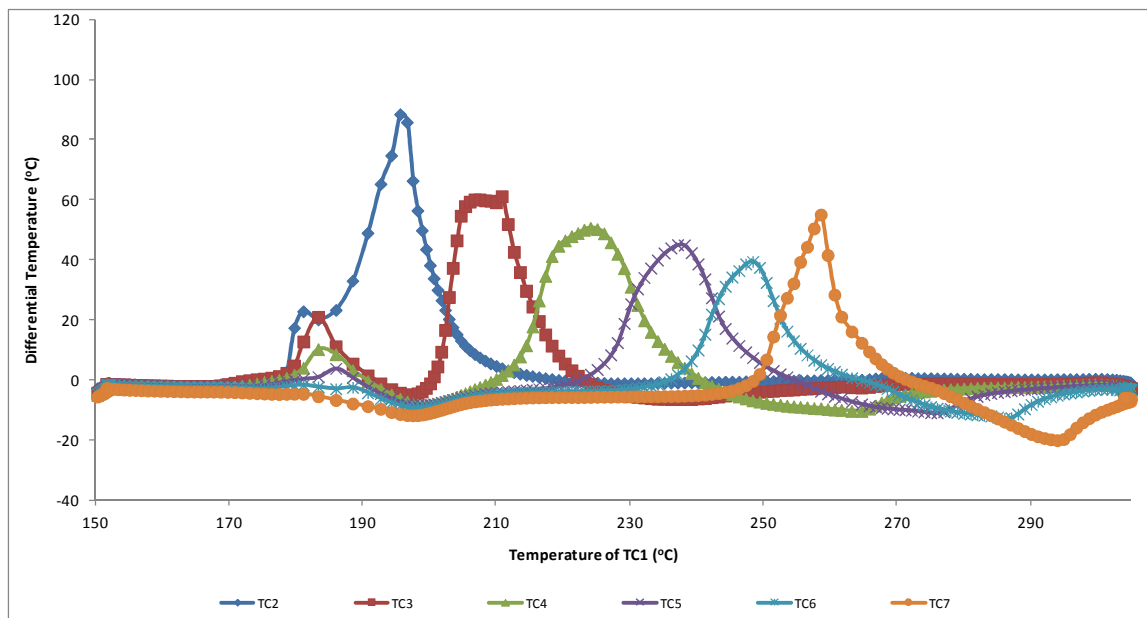


Figure 4-22: Differential temperature with reference to the first thermocouple (TC1) for Test 10 ($n\text{-C}_{15}\text{H}_{32}$, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

4.8 Test 11: Ramped-Temperature Air Injection on $n\text{-C}_{15}\text{H}_{32}$ with No Interstitial Water

A numerical phase behavior study of Oil A (which will be reported in Chapter 6) suggests that interstitial water saturation has a significant impact on the phase behavior of the hydrocarbon phase. The presence of a hydrocarbon/water/gas mixture inside the core affects the vaporization and oxidation/combustion behavior of the hydrocarbon. The core mixture in Test 11 (also Test 13 which is a high flux nitrogen injection test on Oil A) did not include initial water saturation in order to study the effects of the interstitial water.

Test 11 is a high flux air injection test performed on $n\text{-C}_{15}\text{H}_{32}$. As a result of elimination of water in this test, saturation of water was allocated to gas. Figure 4-24 presents the temperature history for this test along with the composition of the produced gas. The plot of differential temperature inside the core (with respect to TC1) is shown in Figure 4-25. The first active zone ignited at 175 °C which is identical to the ignition temperature in

Test 10 that included water. The first gas composition data points for Test 11 were unfortunately missed; however, the product gas composition profile over the remainder of the test showed an essentially constant composition during the period that the oxidation/combustion front moved through the last three zones. Also the shapes of the exothermic peaks for the last three thermocouple locations were very similar.

Table 4-11: Summary of post test core and fluid analysis for Test 10

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	9.93	10.03
<i>Mass of Produced Liquid (g)</i>	7.19	10.89
<i>Recovery (%)</i>	72.39	108.62
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.05	0.20
Mass of Residual Solid (Coke) from Core Ignition (g)	1.34	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	1.36	3.48
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	1.06	7.34
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.7833 at 15 °C, 0.7761 at 25 °C, 0.7655 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	2.7 at 15 °C, 2.14 at 25 °C, 1.52 at 40 °C	
<i>PH of Produced Water</i>	3.38	

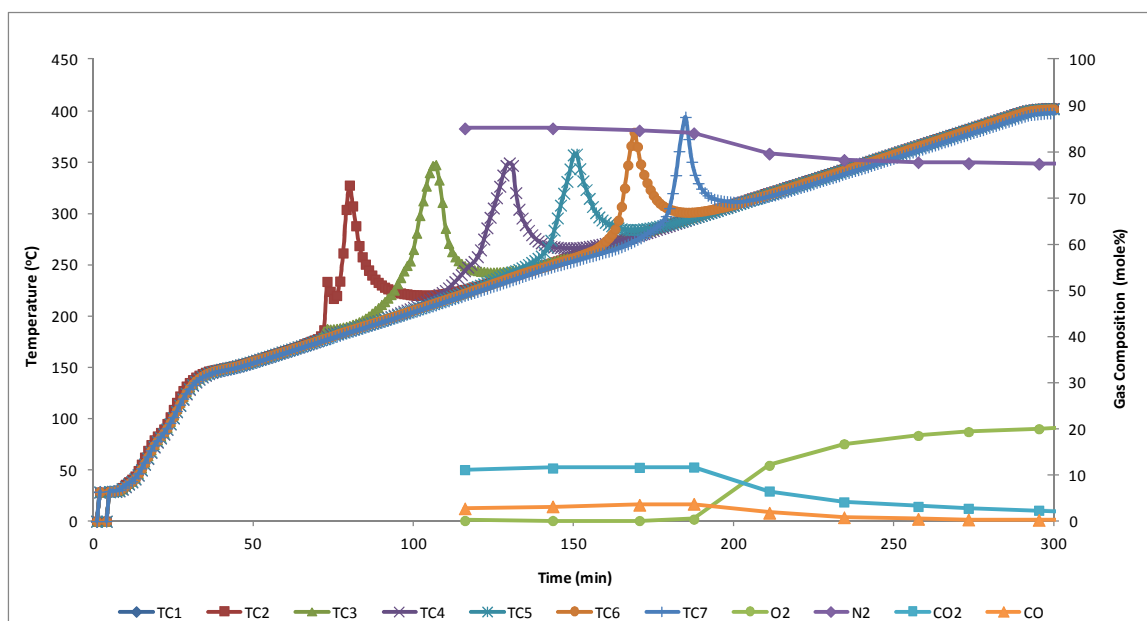


Figure 4-23: Temperature history and product gas composition for Test 11 (n-C₁₅H₃₂, air, 38.2 sm³/m²h, no interstitial water)

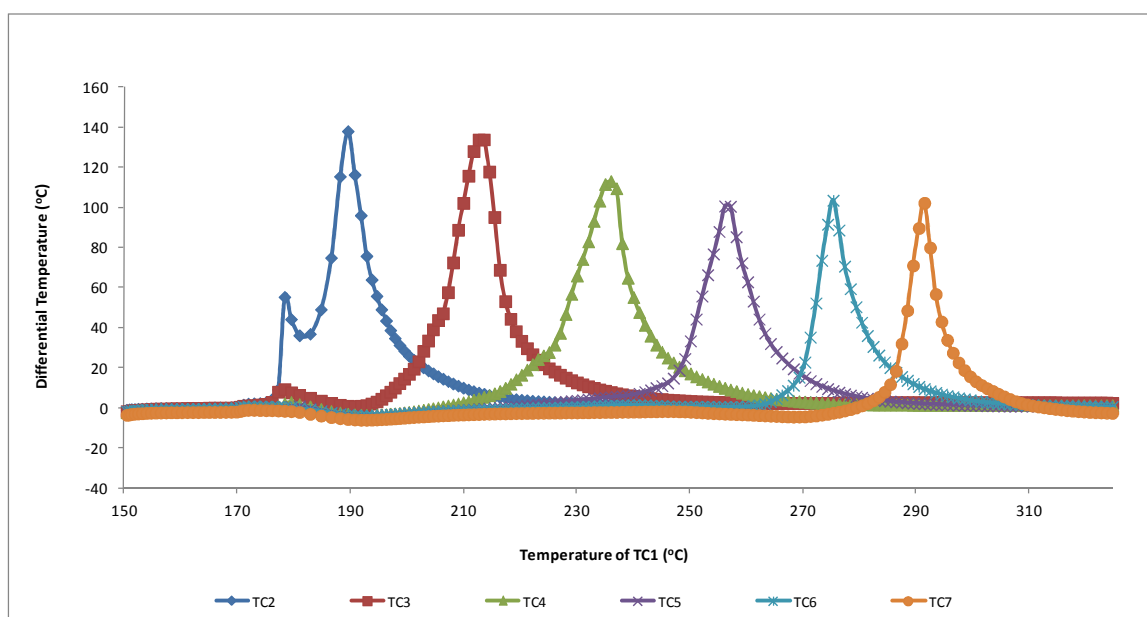


Figure 4-24: Differential temperature with reference to the first thermocouple (TC1) for Test 11 (n-C₁₅H₃₂, air, 38.2 sm³/m²h, no interstitial water)

Table 4-12: Summary of post test core and fluid analysis for Test 11

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	10.99	0.00
<i>Mass of Produced Liquid (g)</i>	7.33	5.56
<i>Recovery (%)</i>	66.70	N/A
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.02	0.10
Mass of Residual Solid (Coke) from Core Ignition (g)	0.47	
Mass of Oil Consumed as Fuel of Combustion (g)	by material balance	by stoichiometry
	3.17	2.74
Apparent Water of Combustion (g)	by material balance	by stoichiometry
	5.56	4.72
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.7849 at 15 °C, 0.7778 at 25 °C, 0.7671 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	2.58 at 15 °C, 2.07 at 25 °C, 1.46 at 40 °C	
<i>PH of Produced Water</i>	2.90	

4.9 Test 12: Ramped-Temperature Nitrogen Injection on n-C₁₅H₃₂

Test 12 was a nitrogen injection test, run at the high injection flux of 38.2 sm³/m²h on n-C₁₅H₃₂. According to the temperature history in Figure 4-25 an evaporation front formed at 125 °C and propagated through thermocouple locations 2 to 7. Following the first front, a second evaporation front formed and was observed at Zone 3 (Figure 4-26) when the first evaporation front was at Zone 6.

Formation of a second evaporation front suggests the existence of a material which is volatile at the temperature of Zone 3 (240 °C). Since the oil packed in Test 12 consisted solely of n-C₁₅H₃₂, which is a volatile medium oil, there still remains some n-C₁₅H₃₂ after the passage of the first front. The residual is then removed during the advance of the second front. This is unlike Test 1, where only the heavy fraction of the oil remained on the core. The two evaporation fronts in Test 12 are very similar in terms of advancement through the core in spite of the difference in the temperature range over which the two fronts propagated.

As was mentioned before, a modification to the liquid collection system enabled measurement of the produced liquid at four separate consecutive time periods for Test 12. The cumulative liquid production for Test 12 is presented along with temperature histories in Figure 4-25.

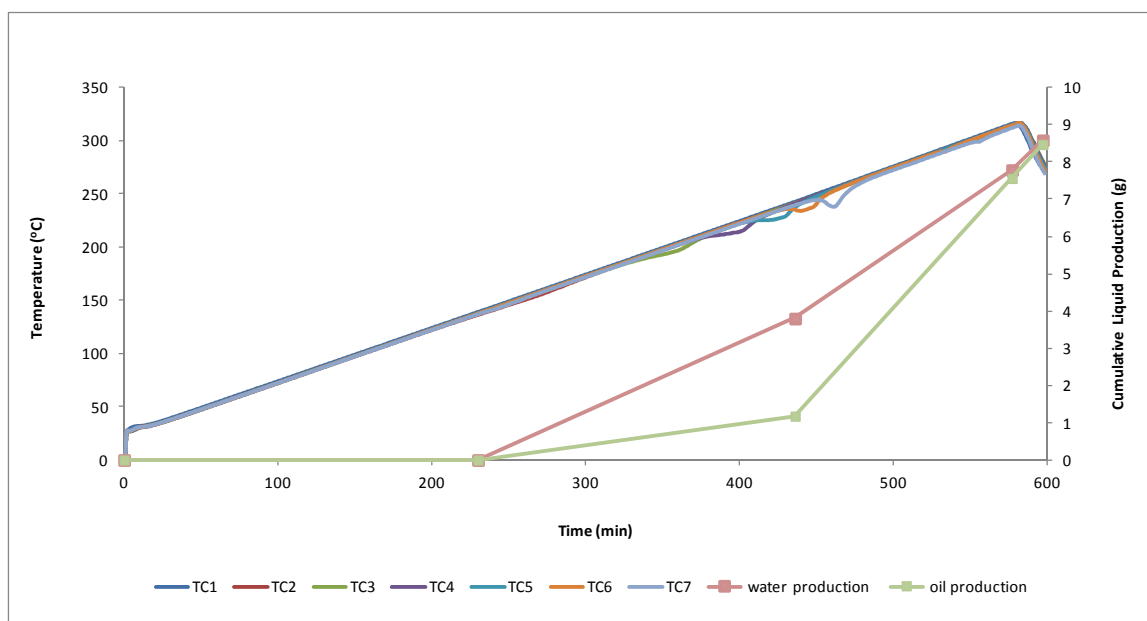


Figure 4-25: Temperature history in Test 12 ($n\text{-C}_{15}\text{H}_{32}$, nitrogen, $38.2\text{ sm}^3/\text{m}^2\text{h}$), and liquid production

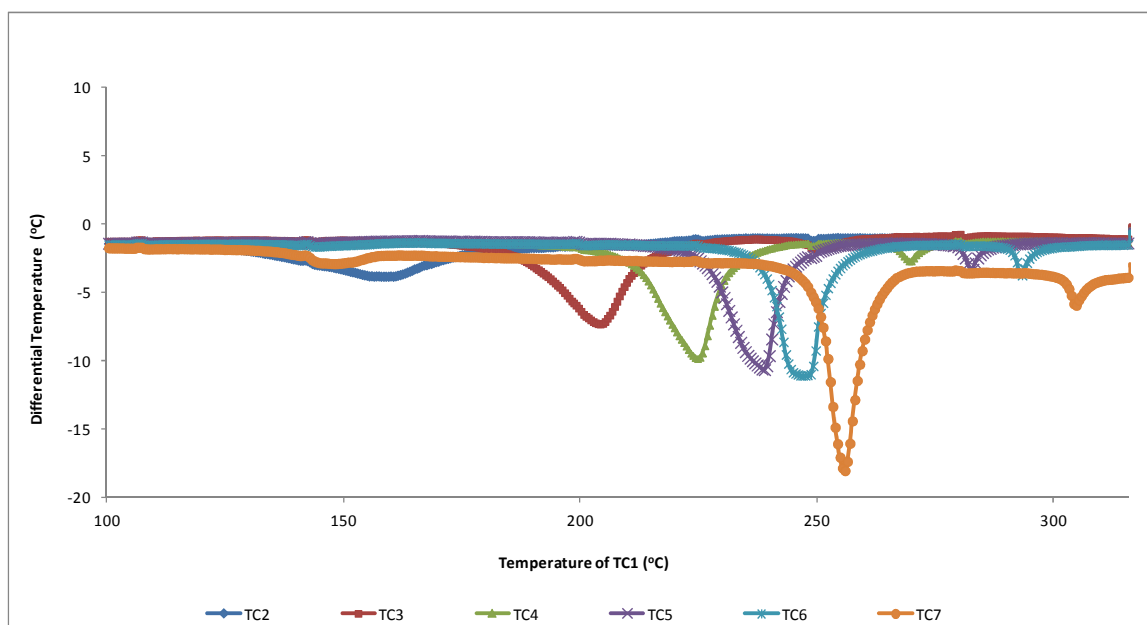


Figure 4-26: Differential temperature with reference to the first thermocouple (TC1) for Test 12 ($n\text{-C}_{15}\text{H}_{32}$, nitrogen, $38.2\text{ sm}^3/\text{m}^2\text{h}$)

Table 4-13: Summary of post test core and fluid analysis for Test 12

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	9.84	9.96
<i>Mass of Produced Liquid (g)</i>	8.47	8.53
<i>Recovery (%)</i>	86.04	85.68
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.01	0.25
Mass of Residual Solid (Coke) from Core Ignition (g)	0.41	
Material Balance Error (%)	Oil	Water
	9.66	11.81
Post Test Liquid Analysis		
<i>Density of Produced Oil (g/cm³)</i>	0.7833 at 15 °C, 0.7761 at 25 °C, 0.7655 at 40 °C	
<i>Viscosity of Produced Oil (cp)</i>	2.70 at 15 °C, 2.14 at 25 °C, 1.52 at 40 °C	
<i>PH of Produced Water</i>	3.38	

4.10 Test 13: Ramped-Temperature Nitrogen Injection on Oil A with No Interstitial Water

In order to determine the contribution of the interstitial water to the formation of an evaporation front, a nitrogen injection test was performed on Oil A in the absence of the interstitial water. No evaporation front could be observed in the temperature history of Test 13 in Figure 4-27. It should be mentioned that the two overall temperature drop events observed around 200 °C and 300 °C were caused by heater's temporary malfunction. Absence of a visible evaporation front in Test 13 indicates that interstitial

water plays a significant role in the development of the evaporation front. Also, as was shown earlier, no evaporation front was apparent from the temperature profiles of air Test 11 which did not include interstitial water (Figure 4-24).

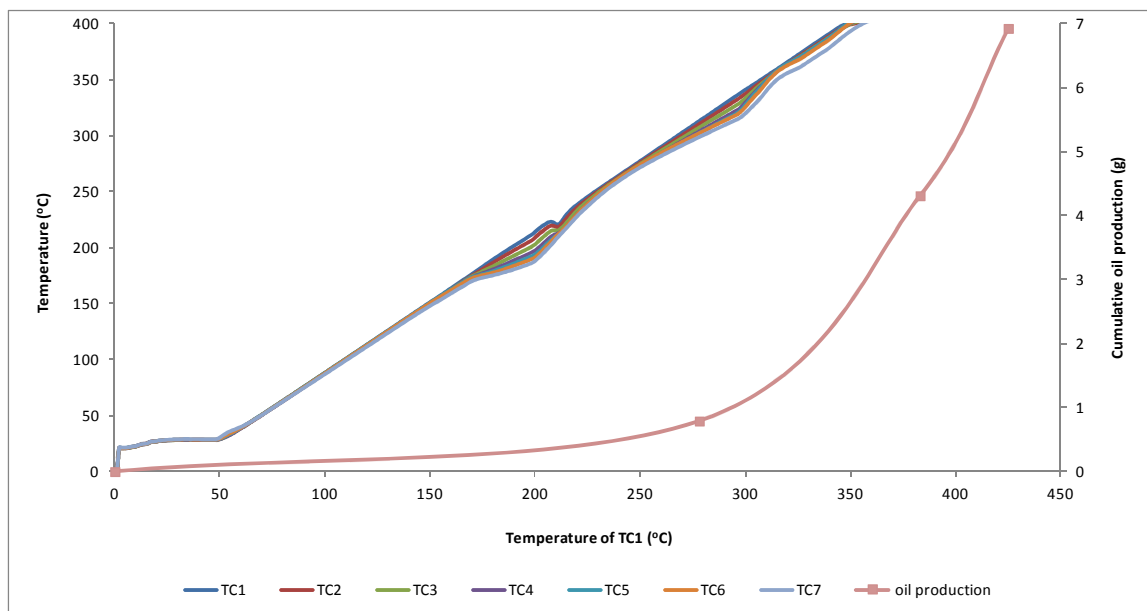


Figure 4-27: Temperature history in Test 13 (Oil A, nitrogen, 38.2 sm³/m²h, no interstitial water), and cumulative oil production

Table 4-14: Summary of post test core and fluid analysis for Test 13

Recovery Analysis	Oil
<i>Mass of Initially Packed Liquid (g)</i>	10.35
<i>Mass of Produced Liquid (g)</i>	7.05
<i>Recovery (%)</i>	68.12
Mass of Residual Liquid from Core Extraction (g)	Oil
	0.65
Mass of Residual Solid (Coke) from Core Ignition (g)	0.72
Material Balance Error (%)	Oil
	18.67

4.11 Test 14: Ramped-Temperature Nitrogen Injection on Water

During the performance and analysis of the high pressure air injection and nitrogen injection tests, it was realized that water has a major impact on both the phase behavior of the fluids in the reactor and also the kinetics of the reactions occurring during these tests in the HPRTO setup. Therefore, Test 14 was dedicated to study the nitrogen-water system as a fundamental experiment to clarify and confirm some findings and observations from the previous tests.

Test 14 was a high flux nitrogen injection test on water where the saturation of the eliminated oil was allocated to the gas phase. Other operational conditions in Test 14 were identical to the rest of high flux nitrogen injection tests (Tests 1, 12, 13), except that for Test 14 the nitrogen injection was started when the reactor was at 60 °C. Also since

the first thermocouple in Test 14 was located in a water saturated zone, in contrast to the other tests, TC1 in Test 14 responded to the endothermic heat of evaporation as shown in Figure 4-28. On the other hand TC7, being located in dry coarse non-saturated sand, exhibited a slight temperature response similar to TC1 in all the other tests. This was due to misplacement of the 40 g silica sand at the production end which was meant to be placed at the injection end.

Since TC1 could no more be treated as a reference thermocouple, in the plot of differential temperatures, Figure 4-29, the differential temperature of each thermocouple was calculated with respect to and plotted against the reactor wall's first thermocouple's temperature.

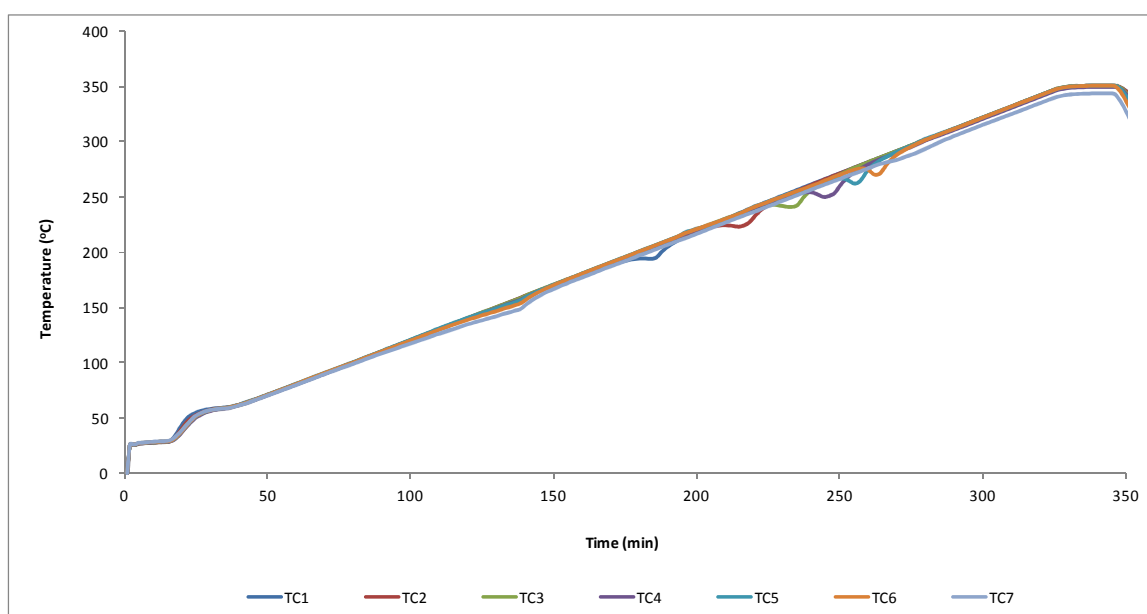


Figure 4-28: Temperature history in Test 14 (Water, nitrogen, 38.2 sm³/m²h)

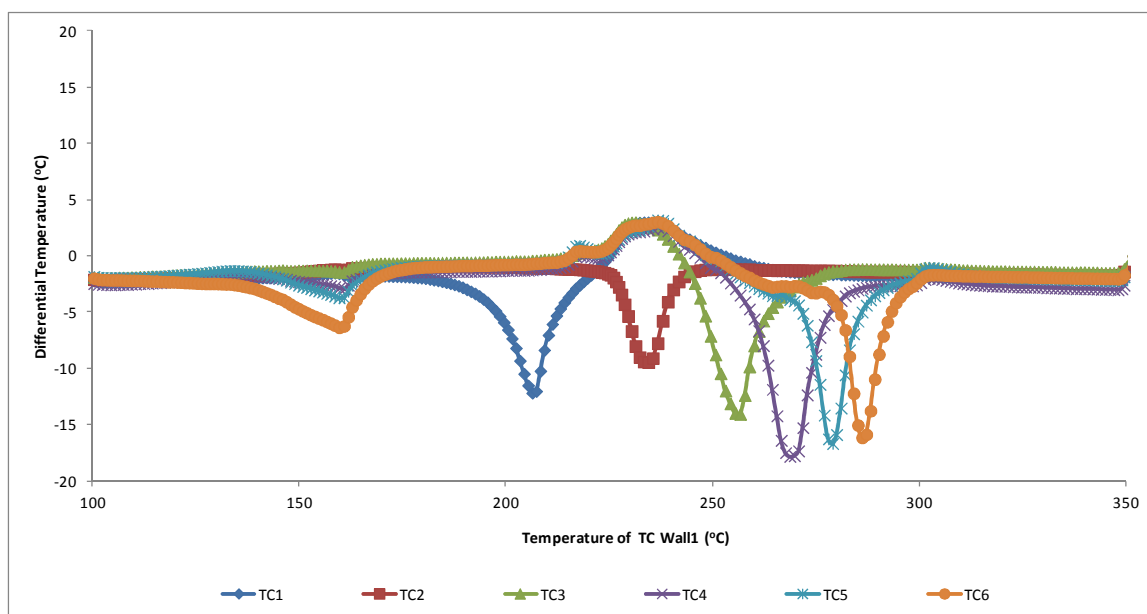


Figure 4-29: Differential temperature with reference to the first wall thermocouple (TC Wall 1), located on the wall of the reactor, for Test 14

As can be noted in both Figures 4-28 and 4-29, an instantaneous operating problem with heaters' power caused a sudden temperature drop demonstrated by all thermocouples around 150 °C.

The evaporation front formed in Zone 1 at the temperature of 160 °C which is very close to the formation temperature of the apparent evaporation front in Test 1 where Oil A was present too. However the extents of the temperature drops in Test 14 in absence of oil were larger.

Table 4-15: Summary of post test core and fluid analysis for Test 14

Recovery Analysis	Oil	Water
<i>Mass of Initially Packed Liquid (g)</i>	0.00	10.67
<i>Mass of Produced Liquid (g)</i>	0.00	9.40
<i>Recovery (%)</i>	0.00	88.09
Mass of Residual Liquid from Core Extraction (g)	Oil	Water
	0.06	0.75
Mass of Residual Solid (Coke) from Core Ignition (g)	1.37	
Material Balance Error (%)	Oil	Water
	0.00	4.89
Post Test Liquid Analysis		
<i>PH of Produced Water</i>	7.88	

Chapter Five: Discussion of the Experimental Results

5.1 Distillation and Its Effects on Kinetics of the Oxidation/Combustion Reactions

This section will employ the results of Tests 1 to 5, as the preliminary part of the experimental study, to characterize distillation not only as a recovery mechanism but moreover as a phenomenon that impacts the kinetics of light oil combustion in HPAI. Distillation or evaporation-condensation of light fractions of oil in thermal processes, more frequently in steam flooding and in-situ combustion, has been studied since its first recognition in 1960. Compositional effect of distillation on phase behavior of light oils, through stripping, and displacement of light ends through evaporation-condensation has been recognized as important. However, certain aspects of distillation such as the latent heat associated with evaporation of hydrocarbons, type of residual fuel remaining in the liquid phase after progression of an evaporation front, and more importantly the type of fuel transferred to the vapor phase through evaporation, all of which impact the kinetics of light oil combustion, has been missing in HPAI studies.

Due to a higher fraction of lighter components in high gravity crudes, these oils are subject to a higher degree of physical compositional changes as compared to heavy oils. In an HPAI process, distillation of lighter components acts as a recovery mechanism and transfers the hydrocarbons through the vapor phase towards the cooler parts of the reservoir. Also it provides the possibility for the hydrocarbons in the vapor phase to engage in combustion reactions, whenever conditions are favorable. This potentially opens a new chapter in kinetic studies of HPAI dealing with vapor phase oxidation/combustion.

In this section, discussions will be mainly drawn from the experimental results of Tests 1,2,3, and 5. The operational details of these tests were reported in Table 3.4. These tests were designed to shed light on the impact of distillation on formation and progression of the thermal front and reaction kinetics associated with the vapor phase oxidation/combustion reactions. The rate of advance of the evaporation and combustion fronts in these tests was found to play a role in these reactions.

5.1.1 Velocity of the evaporation and combustion fronts

Figure 5-1 illustrates the velocity of the evaporation front in Test 1, plotting the axial position of the individual thermocouples against the time that these thermocouples first displayed a reduction in temperature. The nitrogen injection flux was constant ($38.2 \text{ sm}^3/\text{m}^2\text{h}$) for the entire test duration. The linear trend observed during the time that the evaporation front passed through the last three thermocouple locations, when the entire core was at higher temperatures, showed a 0.32 m/h velocity for the front in Test 1.

The rate of advancement of the reaction zone for Test 2 is shown in Figure 5-2. This figure presents a plot of thermocouple locations versus the time at which the individual thermocouples attained a peak temperature. Based on the linear curve on the plot, the average reaction front velocity is 0.19 m/h.

Generally, the velocity of the evaporation fronts were plotted based on the onset of the formation of the endothermic temperature dips, whereas for the combustion fronts the time of the maximum peak temperature has been considered for calculation of the velocity due to a more uniform shape of exothermic peaks in air injection tests. The velocity curves for all evaporation and combustion fronts observed in the 15 Tests are presented in Appendix C while their values are reported in Table C-1.

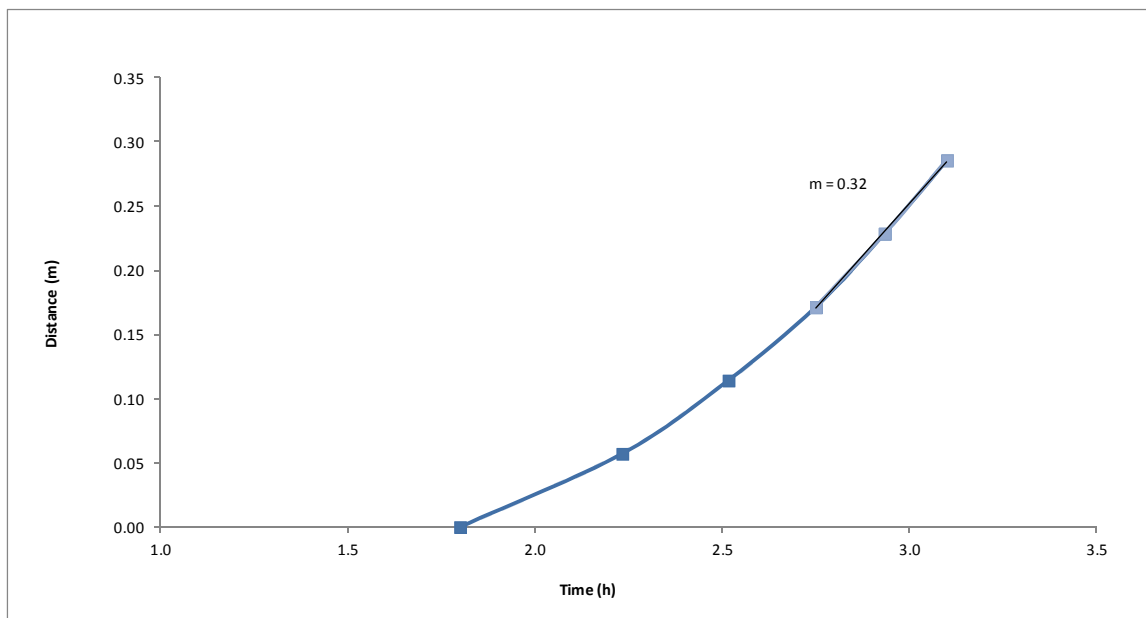


Figure 5-1: Rate of advancement of the evaporation front in Test 1 (Oil A, nitrogen, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

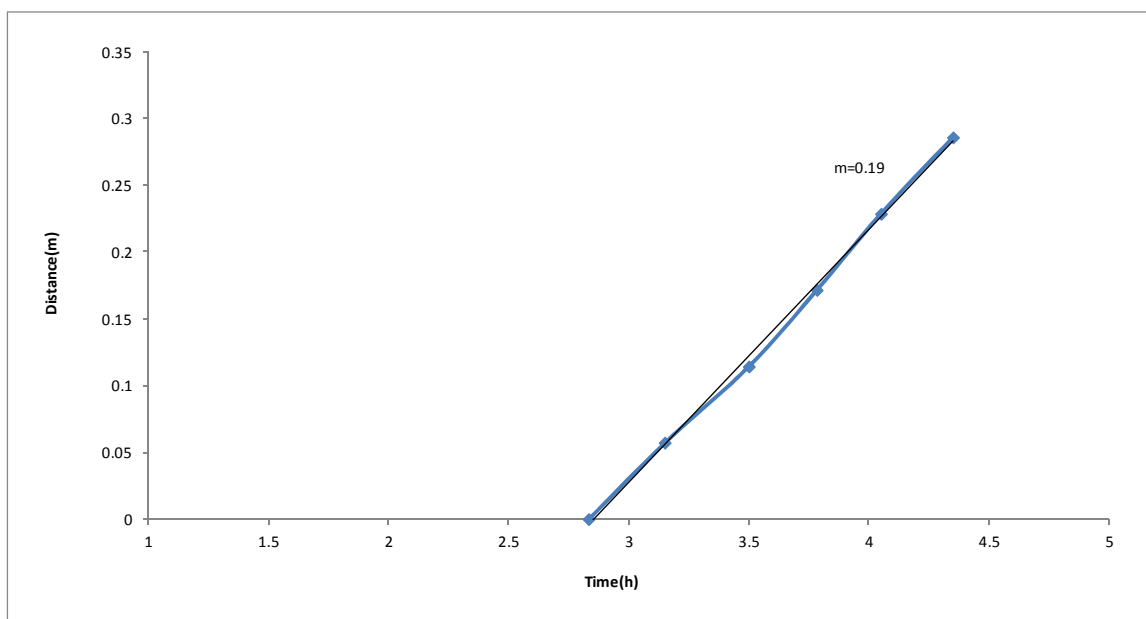


Figure 5-2: Rate of advancement of the combustion front in Test 2 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

The air requirement for an in situ combustion process is defined as the volume of air required to sustain the process per unit volume of the reservoir core:

$$\text{Air Requirement (sm}^3/\text{m}^3) = \frac{\text{Flux (sm}^3/\text{m h)}}{\text{Velocity (m/h)}} \quad 5.1$$

Based on this definition, the air requirement for Test 2 calculates as 200 sm³/m³ of core. This number is only slightly higher than the rule of thumb number of 173 sm³/m³ which is typically assumed for high gravity oil reservoirs and is often observed during combustion tube tests performed on medium to light oils. Similar to Test 2, the propagation velocity of the reaction zone for Test 3 was calculated by plotting the thermocouple locations against the time at which the individual thermocouples attained a peak temperature (Figure 5-3). The average combustion front velocity for Test 3 was 0.21 m/h, which based on Equation 1 yields an air requirement of 176 sm³/m³.

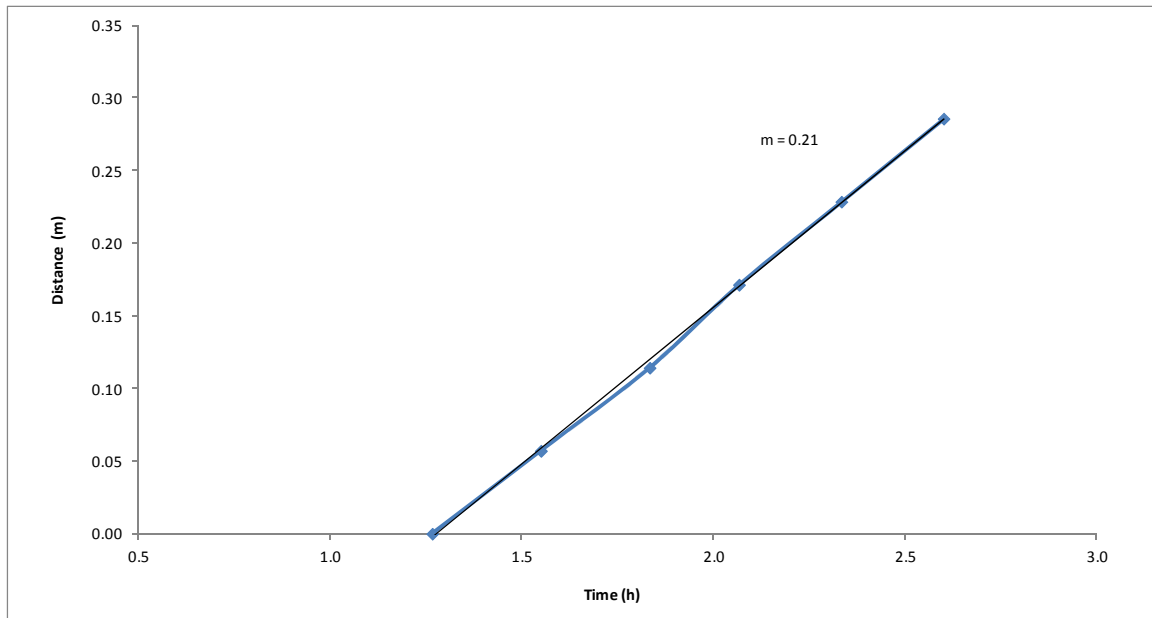


Figure 5-3: Rate of advancement of the combustion front in Test 3 (Oil A, air, 38.2 sm³/m²h)

The velocities of the combustion fronts in Test 2 and Test 3 were very similar (0.19 m/h and 0.21 m/h respectively). Also they were very close to the velocity of the combustion front in Test 4 which was 0.17 m/h (Appendix C). This observation indicates that the rate of delivery of air in the HPRT0 tests is a dominating factor. Since the rate of air injection in the mentioned tests were identical, although preheated to different temperatures these tests exhibited very similar propagation velocities for the thermal (combustion) fronts. This means that once the thermal front was established, the rate of its propagation was directly dominated by the supply of air. Nevertheless it should be mentioned that Tests 2, 3, and 4 had similar phase behavior, all being conducted on the same mixture of Oil A and water.

The velocity of the evaporation front for the isothermal nitrogen injection Test 5 is demonstrated in Figure 5-4. The linear advancement of the front indicates a constant low

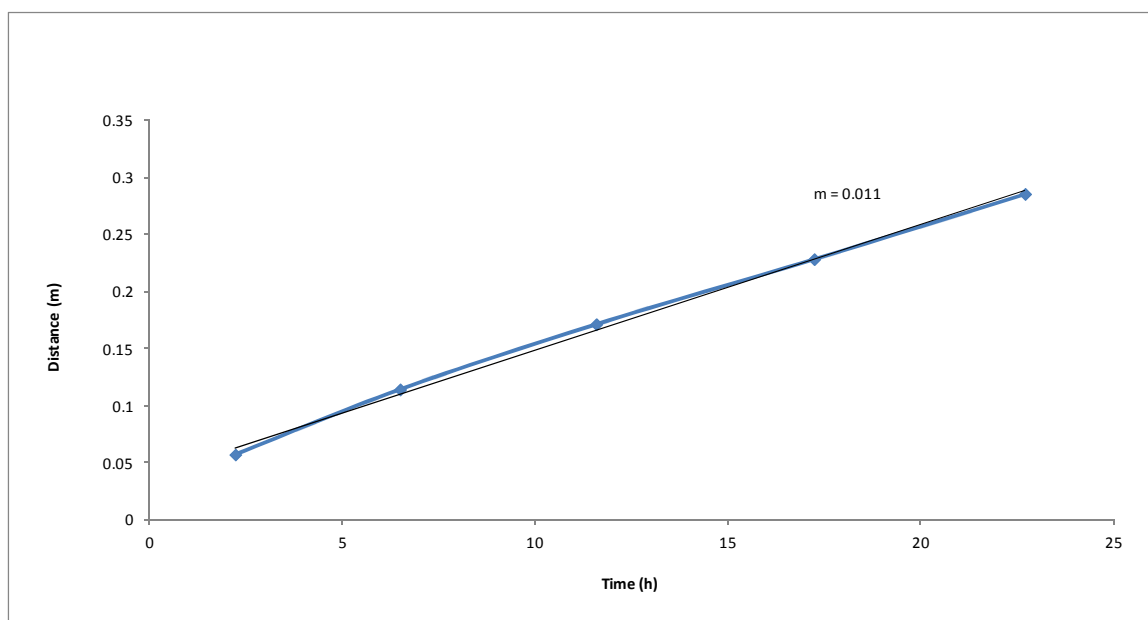


Figure 5-4: Rate of advancement of the evaporation front in Test 5 (Oil A, isothermal nitrogen, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

velocity (0.01 m/h) for the front which reflects the saturation of the injected nitrogen with vapor at the time of the endothermic dips.

5.1.2 Evaporation Front Propagation

The nature of the evaporation front in the high flux nitrogen injection test (Test 1; Figure 5-1) is reflective of the mixture's phase behavior and also the extent of dependency of the evaporation rate on the controlling mechanisms. In Figure 5-5, the rate of change of velocity with temperature has been illustrated for both the evaporation front in the nitrogen injection Test 1 and the flow of interstitial gas (injected nitrogen). Based on the slopes of linear trend line curves shown on the plot, the rate of change of the evaporation front's velocity with temperature is very similar to the rate of change of the interstitial nitrogen velocity with temperature. This implies that the velocity of the evaporation front is dominated by the saturation of the injected gas.

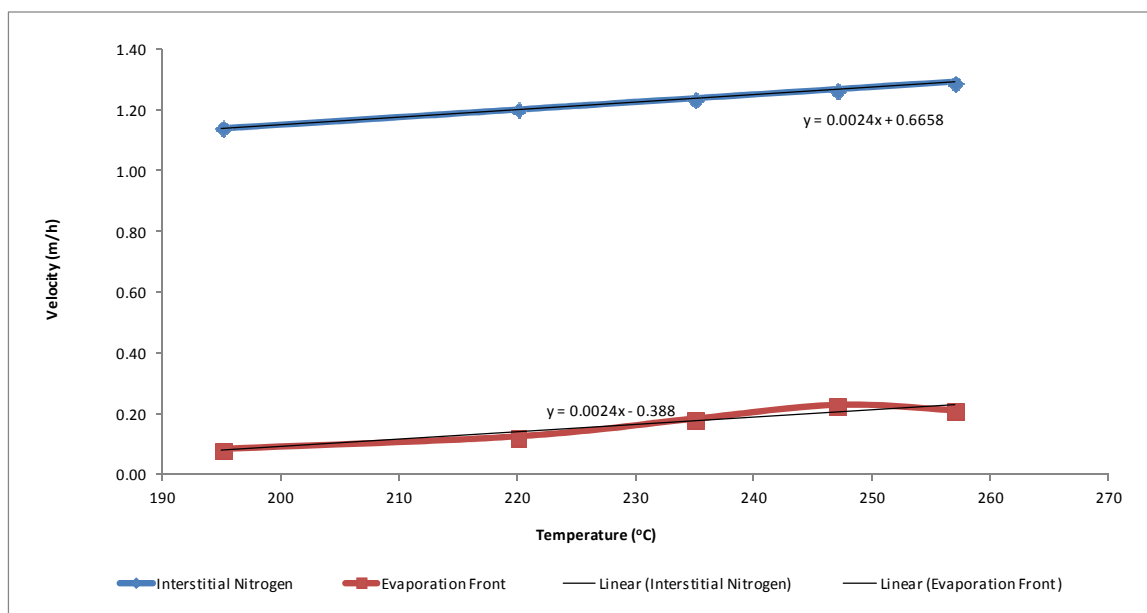


Figure 5-5: Rate of change of velocity with temperature for the evaporation front in Test 1 with reference to rate of change of velocity for interstitial nitrogen

Moreover, the orderly propagation of the endothermic evaporation front (Figure 4.2) suggests that each zone inside the reactor exhibits the endothermic heat of evaporation only after the evaporation front has already passed through the previous zone. This indicates that the injected gas is saturated up to the time that the temperature drop occurs at each thermocouple location. In other words, the evaporation phenomenon inside the HPRT reactor is saturation-controlled rather than being diffusion-controlled and distillation is not necessarily mass transfer limited in this case.

The extent of the temperature drop associated with the endothermic heat of evaporation varies with temperature throughout the reactor zones. Although not very clear in Figure 4-2 (Due to the axial heat transfer), the temperature drop has an increasing trend with time. This is reflective of the rate of evaporation of the oil and water molecules which in turn depends on the oil-water-gas mixture's phase behavior. As reactor temperature ramps with time, more molecules evaporate dictated by the phase behaviour.

In Figure 5-6, velocity of the evaporation front in the nitrogen test (Test 1) and the velocities of the combustion fronts in the air injection tests (Tests 2 and 3) are presented in the same graph. In this graph the velocity of propagation through the first three zones (zones 2, 3, and 4) are plotted separately from the last three zones, as there is a distinct change in the slope of the linear curves (velocities) when the fronts pass through Zone 4 towards Zone 5. The evaporation front of Test 1 in this figure approaches a constant velocity while passing through the last three zones. As it was observed in Figure 5-1 (section 5.1.1), the experimental temperature data of Test 1 showed that the velocity of the evaporation front follows an increasing trend while passing through the first four thermocouples. However, it reached a plateau during the last three zones and this was indicated by the linear trend line in Figure 5-1 which can also be seen in Figure 5-6.

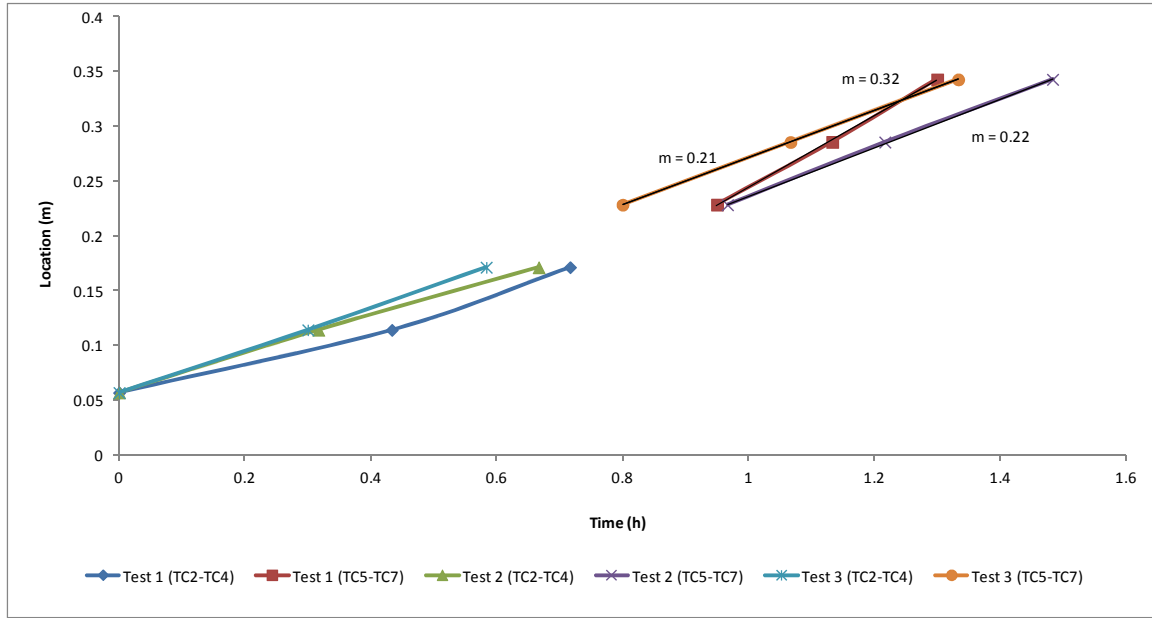


Figure 5-6: Velocity of the evaporation front in Test 1 and combustion front in Test 2 and Test 3

If the period of time during which the velocities show a change are correlated back to the temperature ranges in the differential temperature profiles (Figures 4-2, 4-4, and 4-7), it is noticed that the velocity changes occur around 250 °C for the mixture of Oil A and water. Theoretically, the velocity of the evaporation front depends on how fast the flowing gas is saturated by the liquid phase which in turn depends on the phase behaviour or K-values of the liquid-gas mixture. Figure 5-7 shows the trend of increasing of K-value with temperature at a constant pressure based on the following correlation.

$$k(P, T) = \left(\frac{a_1}{P} + a_2 + a_3 P \right) \frac{a_4}{T - a_5} \quad 5.2$$

Now, at a constant pressure and assuming a value of one for the coefficient a_4 and zero for a_5 , the general trend of the K-value with temperature follows a function in the form

of τ . Basically, the exponential function approaches a plateau at high temperatures, thus dictating very close numbers for K-values during these temperatures.

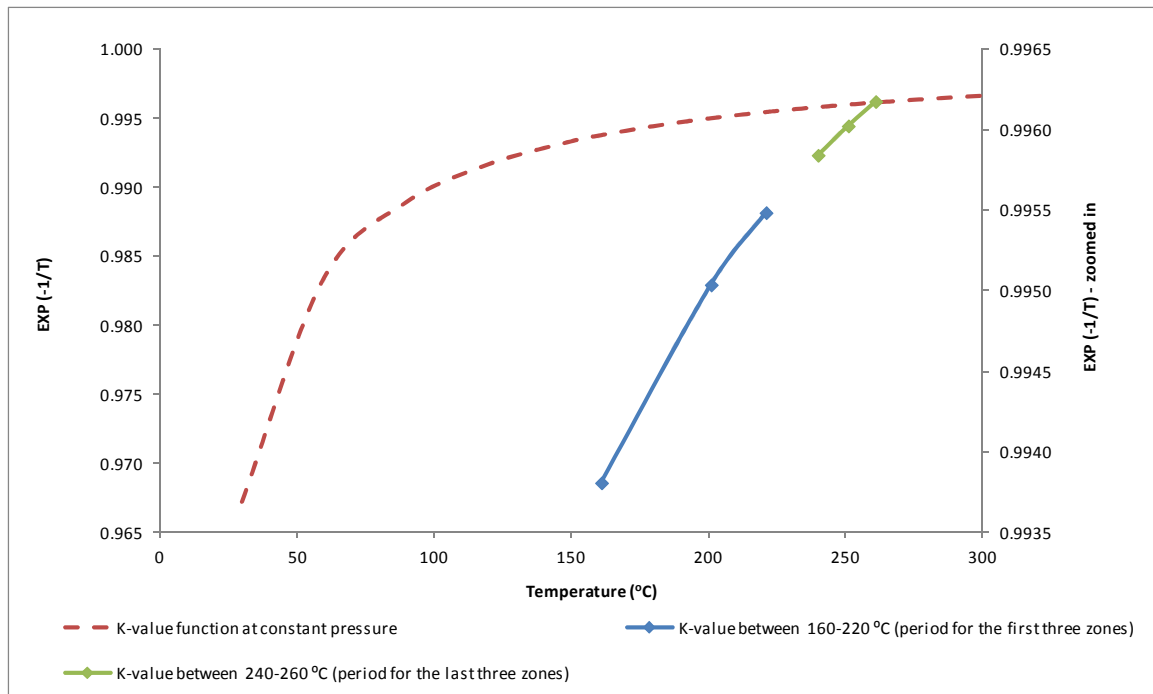


Figure 5-7: General form of K-value changing with temperature, during the temperature period of the HPRT0 tests

The right axis on Figure 5-7 highlights the K-values over the temperature range where the internal thermocouples in the individual zones show a reaction to the advance of the evaporation and combustion fronts. In this plot, the curve for the last three zones, in green, has been separated from the rest in blue. It can be noticed that the K-value during the temperature period of the last three zones shows a very slight change, thus similar evaporation behavior is expected in these zones. This is in line with the observations from Test 1 (Figure 5-1 and Figure 5-6) where velocity of evaporation reaches a constant value at temperatures above 250 °C.

Also in Figure 5-6 it can be observed that the rate of advance of the evaporation front in Test 1 and combustion front in Test 2 and 3 are very close. This implies a co-occurrence of evaporation and combustion in HPRT0 tests which will be more clarified in the following section.

5.1.3 Vapor Phase Oxidation/Combustion

Classical in-situ combustion literature dealing with heavy oils generally assumes that a solid residue (coke) is the fuel consumed during an air injection process. More recent papers (Tingas *et al.*, 1996; Moore *et al.*, 1998; Clara *et al.*, 1999; Kuhlman *et al.*, 2000) dealing with higher gravity oils include a light oil component with no specific reference to the reactions occurring in the “vapor phase”. Observations in this current study suggest the participation of the vapor phase in the combustion reactions occurring in the HPAI process. In fact, whether or not the composition of the hydrocarbon in the vapor phase falls in the right range (flammability range), plays an important role on combustion kinetics of HPAI.

In air injection tests (Tests 2 and 3) a distinct evaporation front is not visible in the temperature profiles; however, the last two thermocouple zones demonstrate a temperature drop prior to displaying the exothermic combustion peaks. This implies that evaporation of the liquid phase and combustion of the fuel occur simultaneously at each thermocouple zone inside the reactor and the small endothermic evaporation temperature dips are masked by the exothermic combustion temperature peaks. However, since the velocity of evaporation increases with temperature (as evident in Figure 5-1), the last two zones show evaporation a few minutes earlier than the combustion peak (Figures 4-4 and 4-7). If the velocity of the visible evaporation front between the last two zones is calculated, the values for Test 2 and Test 3 are both 0.34 m/h, which is very close to the velocity of the evaporation front in Test 1 (0.32 m/h).

In order to better picture this phenomenon, the temperature profiles of Test 2 and Test 3 are put together with the temperature profile of Test 1 (nitrogen test) on the same graph in Figure 5-8 and Figure 5-9 respectively. These figures demonstrate the similarities between the evaporation and combustion front velocities. This is the reason why the evaporation front is veiled by the exothermic peaks in the air injection tests. It also implies that while the evaporation front propagates along with the combustion front, it feeds the combustion zone with at least part of the vapor phase fuel involved in oxidation/combustion reactions. The same results were observed when the temperature history of Test 10 and Test 12 were compared to each other in Figure 5-10.

Observations from the tests discussed in this section are particular to the operational conditions of these tests and a change in some parameters such as gas injection flux or composition of the mixture, which will be discussed in the next sections, will affect the results. However, none of the tests rule out the potential participation of vapor phase in oxidation/combustion reactions whenever the conditions are favorable; i.e. where the composition of the hydrocarbon in the vapor phase falls in the flammable range at the same location that oxygen is present.

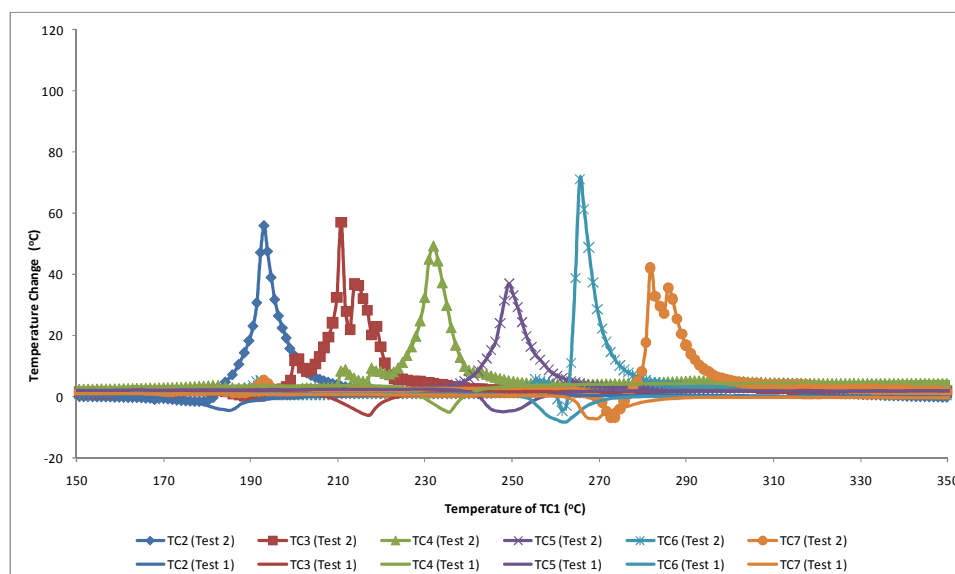


Figure 5-8: Differential temperature with reference to TC1, as observed at thermocouple locations during Test 1 (Oil A, nitrogen, 38.2 sm³/m²h) and Test 2 (Oil A, air, 38.2 sm³/m²h)

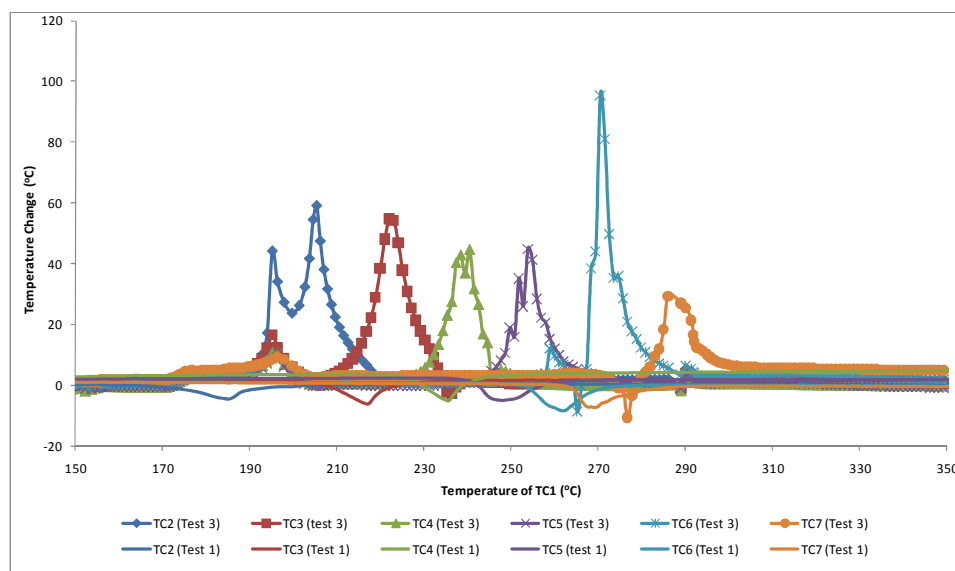


Figure 5-9: Temperature change with reference to TC1, as observed at thermocouple locations during Test 1 (Oil A, nitrogen, 38.2 sm³/m²h) and Test 3 (Oil A, air, 38.2 sm³/m²h)

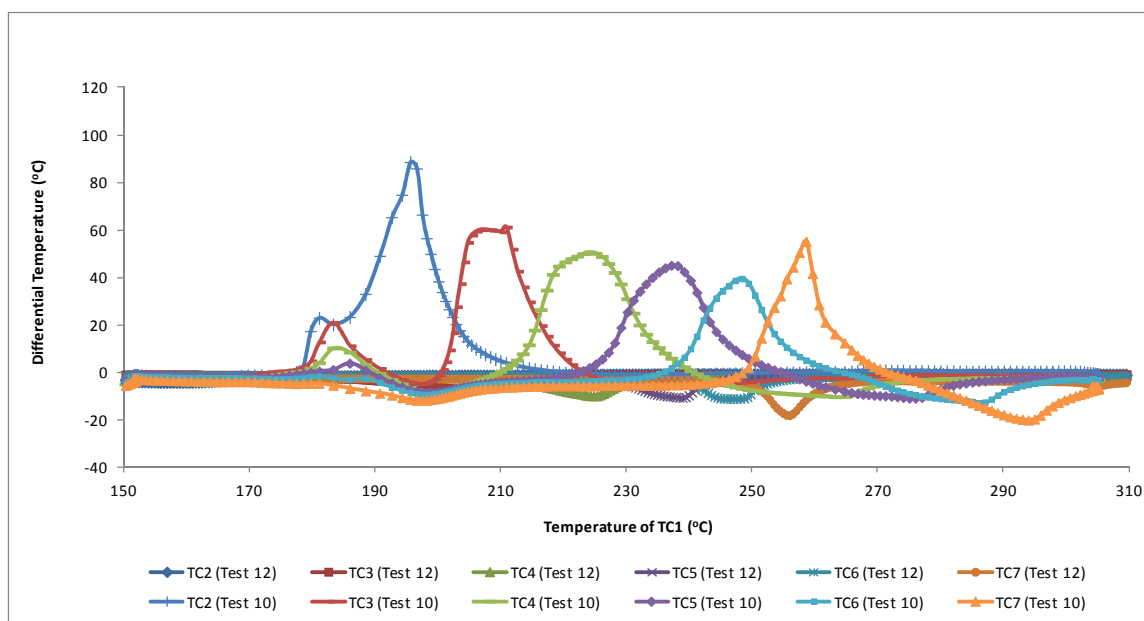


Figure 5-10: Temperature change with reference to TC1, as observed at thermocouple locations during Test 12 ($n\text{-C}_{15}\text{H}_{32}$, nitrogen, $38.2 \text{ sm}^3/\text{m}^2\text{h}$) and Test 10 ($n\text{-C}_{15}\text{H}_{32}$, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

5.2 Effect of Air Flux on Oxidation/Combustion Behavior in HPAI

Section 5.1 described, based on experimental data of Tests 1-3, how hydrocarbon in the vapor phase gets involved in the oxidation/combustion reactions. In this section it will be discussed how the flux of air can influence the outcome of an air injection process, through analyzing the results of the Tests that were performed under a lower flux. As it was discussed in Chapter 4, air injection Test 6 and 15, and nitrogen injection Test 7 were designed to be conducted under an air injection flux as much as $1/3$ of the base flux of $38.22 \text{ sm}^3/\text{m}^2\text{h}$ that was used for the rest of the tests. However, Test 7 was flowed at a higher than expected flux due to a calibration problem with the mass flow meter. So, the injection flux for Test 6 and 15 was $12.75 \text{ sm}^3/\text{m}^2\text{h}$, while it was $25.2 \text{ sm}^3/\text{m}^2\text{h}$ for Test 7.

Results in this section will be drawn based on the experimental oxygen utilization data, temperature data, and production data in addition to simulated distillation data of the produced oil in the low flux tests. However, prior to investigation of the experimental data obtained from the low flux tests, a very important concept which plays a key role in understanding the combustion behavior in the gas phase needs to be reviewed. The theory of “flammability limit/range” is a fundamental concept of gas phase combustion in the mechanical engineering profiles dealing with the internal combustion engines.

5.2.1 Flammability of Gas and Vapor Hydrocarbons

As for conventional gas phase combustion or combustion of liquid fuels in gasoline or diesel engines, in order for the vapor phase to participate in the combustion reactions, the concentration of the vapor hydrocarbon at a given air injection flux, pressure, and temperature must fall in the “flammable range”. If the concentration of the fuel in the vapor phase is outside the flammable range, combustion reactions cannot be supported in the vapor phase. However, depending on the temperature, oxidation reactions involving the liquid phase or residual solid phase can be active.

Under given physical conditions there are both fuel “lean” and fuel “rich” limits. Only within these limits, self-propagation of the thermal front can occur. In mechanical gas combustion engineering, the limits depend on the direction of front-propagation and dimensions of the employed vessel. It is not fully developed whether measured flammability limits are fundamental properties of a combustion system, independent of the set-up and apparatus and have absolute limits. However, as long as the experimentally determined limits are obtained under conditions similar to those found in practice, they are representative (J.W. Rose and J.R. Cooper, 1977).

The flammability limits may change with pressure, temperature and existence of inert gases in the mixture. An increase in the temperature or pressure of most combustible oxidant systems widens the limits of flammability; although, the lower limit of flammability or the lean side is not as sensitive to these parameters as the upper limit or the rich side. Higher temperatures result in lower lean limit and higher rich limit, while higher pressures increase both limits. Addition of a diluent tapers the limits, largely due to a reduction in the upper limit. At the lean side the component in excess which also serves as a diluent is oxygen. So, replacing it with another diluent, such as nitrogen, does not alter the physical properties of the system due to closeness of the average thermal and diffusion properties of oxygen and gas diluents such as nitrogen. In general, the rich limit is more complex than the lean limit, because at the upper limit excess fuel is the diluent which may go under pyrolysis to give new products which may result in generation or absorption of heat. There are a number of empirical correlations to predict the flammability limits of a mixture at different temperatures and a constant pressure. But, the effect of an increase in pressure at constant temperature on the flammability limits is neither simple nor uniform. The non-uniformity of the effect of pressure arises from its combined influences on heat losses and reaction rates which may counteract. Prediction of the flammability limits of a mixture of n number of flammable gases with mole fractions of x_i in air can be carried out within reasonable accuracy using Le Chatelier's rule (J.W. Rose and J.R. Cooper, 1977):

$$limit_{mixture} = 1 / \sum_i^n (x_i / limit_i) \quad 5.3$$

The classical gas combustion literature, classifies the flames formed and developed by the oxidation/combustion reactions in two categories: conventional flames, and cool flames. Cool flame is a flame having maximal temperature below 400 °C (Lindström *et*

al., 2009). Contrary to conventional flames, the reactions in the cool flame are not vigorous and release very little heat, light, and carbon dioxide. A cool flame has an induction time which shortens as the pressure increases. A typical temperature increase upon ignition of a cool flame is a few ten degrees centigrade whereas it's in the order of a thousand for the conventional flames (Pearlman, 1999 and Jones, 2003).

Composition range for the conventional flames centers on the theoretical value (stoichiometric air/fuel ratio) for the complete combustion of the mixture. However, the composition of a cool flame ranges further from the stoichiometric ratio and on the slower sides of the combustion reactions, where air/fuel ratio is frequently 1/1 (J.W. Rose and J.R. Cooper, 1977). Cool flames require a source of controlled temperature, usually 300-400 °C. Rose and Cooper (1977) in their book, *Technical Data on Fuel*, argue that owing to the existence of cool flames at elevated temperatures, the rich limit of flammability often increases drastically and unpredictably with a slight increase in temperature. Fig 5-11 shows the variation of the flammability limits of conventional and cool flames with pressure. Line A is passed at the same pressure through regions that, based on the air/fuel ratio of the mixture, can possibly propagate a cool or conventional or no flames.

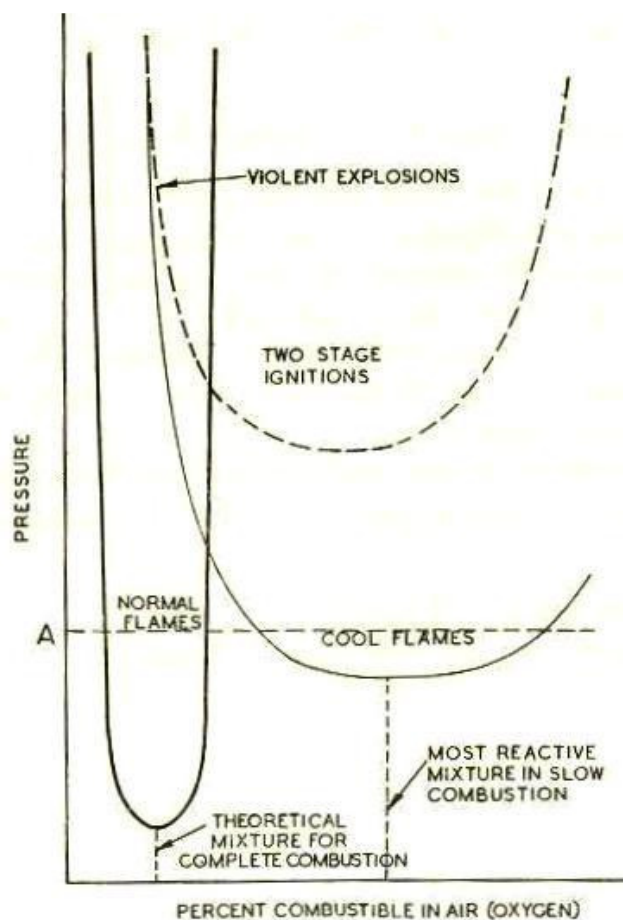


Figure 5-11: Variation of the flammability limits with pressure; courtesy of J.W. Rose and J.R. Cooper, 1977

As diagrammatically shown in Figure 5-11 cool flames form at the (fuel) rich side of the flammability range. A cool flame is reported to be the combination of free radical oxygenated compounds (RO^*) to form formaldehydes. Cool flames have been observed for all hydrocarbons and for any molecular weight greater than that of ethane, formation of cool flame is likely in the range of 260- 400 °C.

From every characteristic reviewed of cool flames, one can elaborate that cool flames in the gas phase are close to oxygen addition reactions in the oil phase. Temperature

profiles of high flux air tests on Oil A (Tests 2, 3, and 4) show a sudden and rapid increase in peak temperature at 260 °C in Zone 6. This can be an indication for explosion of the cool flame in the gas phase. This condition is marked as “violent explosions” in Figure 5-11 and implies that the vapor mixture is approaching stoichiometric condition. Since the amount of oxygen uptake is almost uniform during the passage of the thermal front, this implies the reaction of a very different generated component. It should be mentioned here and will be shown in Chapter 6 that as the thermal front passes through the reactor zones, the concentration of the vapor hydrocarbon increases and the mixture of air and fuel becomes more fuel rich.

Basically, when a thermal front becomes visible during an HPRTTO test it does not necessarily reflect the onset of the oxidation/combustion reactions. Rather, it indicates that at that particular time and location, the thermal energy of the system is sufficient to raise the temperature of the system above the lower sensitivity limit of the thermocouples (1 °C for HPRTTO design). At a given location, the heat conservation equation includes axial conduction and convection heat transfer terms, conduction heat transfer to the reactor wall as well as the copper mandrel and generation of heat by the oxidation/combustion reactions. The onset of the oxidation/combustion reactions is earlier than the apparent time that it becomes visible through the formation of a thermal front. From the GC data, it is realised that the oxygen concentration inside the reactor drops below its original value, at least 30 minutes before the first sign of an evident temperature change by the thermocouples.

A standard heating value suggests the energy generation of 3716 kJ for each standard cubic meter of consumed air. Oxygen consumption data (Appendix D) for all 15 HPRTTO tests show that formation of a visible thermal front is associated with at least 70% utilization of oxygen. As the front advances, this number increases to values as high as

100%. This implies that in order to reach a positive accumulation of energy inside the reactor, and consequently formation of the thermal front, at least 70% of the injected oxygen should be consumed in the high flux tests and 95% in the low flux ones.

In Chapter 4 it was reported that the oil recoveries from the low flux air Tests 6 and 15 were around 25% less than the recovery for high flux air Test 3 which, excluding the lower injection flux, had the same operational conditions. The exothermic front in the low flux tests developed at a higher temperature than the high flux tests. In general, in a low flux test, the amount of hydrocarbon that can be carried with the flow of air is less, thus the rate of evaporation is less. Consequently the temperature at which sufficient hydrocarbons have evaporated to establish the air/fuel ratio in the gas phase within the flammable range is higher than that for the high flux tests. Also, in the high flux nitrogen Test 1 and low flux nitrogen Test 7 (Figures 4-2 and 4-20, respectively) the onset of the evaporation front is observed to be at a higher temperature for the low flux test and the dips are smaller in this test, which also is a result of faster saturation of air in a low flux test. The longer period of time before the thermal front forms in the low flux Tests 6 and 15, subjects the oil to a greater degree of oxidation addition reactions at lower temperatures and hence, a lower recovery. Figures 4-16 and 4-19 which showed the production gas history for Tests 6 and 15 respectively also show a very slow build up of oxygen after the thermal front has passed through the entire core. This time period for the low flux tests is almost three times longer than was experienced in the high flux tests. This is indicative of more solid residual as a result of the extensive oxygen addition reactions, due to richness of the fuel in these low flux tests. Also the richness of fuel in the low flux Test 6 is implied by the clipped off shape of the temperature peaks (Figure 4-16). This phenomenon is not as obvious in Test 15, since this test included 30% less initial oil than that in Test 6 (caused by an unplanned change in the size of the reactor).

The atomic H/C ratios, which will be discussed in detail in Section 5.5, for the low flux Tests 6 and 15 also support the high amount of solid residual formed in low flux tests.

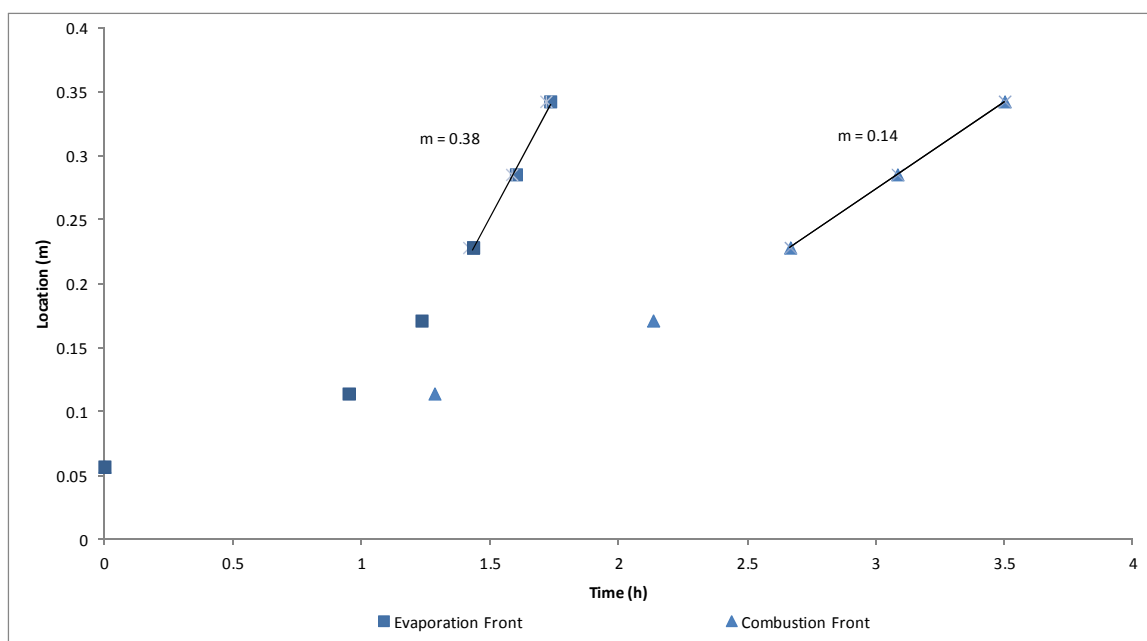


Figure 5-12: Rate of advancement of the evaporation and combustion fronts in Test 15 (Oil A, air, $12.7 \text{ sm}^3/\text{m}^2\text{h}$)

Figure 5-12 plots the axial position of the individual thermocouples against the time that these thermocouples first displayed a change in temperature during the low flux air Test 15. The slopes of the linear curves shown on the plots represent the propagation velocity of the evaporation and oxidation/combustion fronts. According to the heating history of Test 15 (Figure 4-18), the visible evaporation front does not coincide with the thermal front and it advances through the entire reactor before the thermal front reaches the second zone. In order to compare the velocities in a single graph, time zero corresponds to the onset time for the individual fronts. It should be noted that the onset times are not the same.

The velocity of the visible evaporation front, when passing through the last three thermocouple locations, was 0.38 m/h. This is almost twice the velocity of the evaporation front in the previously reported high flux tests. Since the onset of the evaporation front in Test 15 is at a higher temperature than that of the high flux tests, the rate of evaporation over this higher temperature range is increased as the K-values increase according to Equation 5.2, thus resulting in a greater velocity for the evaporation front. The rest of the zones in Test 15 (Zones 3-7) burn on heavier hydrocarbons which evaporate at higher temperatures than those experienced in high flux tests. Also a large quantity of oxygenated products which later crack into a heavy residual get involved in the combustion reactions while the thermal front passes through the last zones. This will also be shown in Section 5.5 using the calculated atomic H/C ratio of the fuel. However, since all the water is evaporated within the first (visible) evaporation front, the second evaporation front (of the heavier hydrocarbons) is not visible as a consequent of not benefiting from the latent heat of water.

It was noted in Figure 5-5 that the rate of change of velocity of the evaporation front with temperature was essentially identical to the rate of change of interstitial velocity as observed for high flux tests. However, the data suggests that the rate of transfer of components from liquid to vapor phase in a low flux test is controlled by mass transfer in the core. Velocity of the thermal front in high flux tests is almost linear, but in the low flux tests it's only linear through the last three zones. This means that oxidation/combustion front velocity is no more solely controlled by the supply of air in the low flux tests. But richness of the fuel for a longer period, and thus production of more oxygenated compounds which form a heavy solid like film may cause a diffusional barrier. Later at higher temperatures, thermal cracking and oxygen induced cracking

reactions may break the film and enhance the rate of transfer of fuel into the vapor phase.

5.3 Effect of Interstitial Water Saturation on Oxidation/Combustion Behavior in HPAI

The presence of interstitial water, more specifically the constant increase of its concentration in the vapor phase as temperature increases in response to the heating ramp, highly impacts the flammability range of the mixture in terms of its dilution effects. However in Test 11 (Figure 4-23), it is seen that in the absence of interstitial water, once a near stoichiometric condition is achieved (starting at Zone 4), that condition is maintained in the vapor phase leading to the uniform propagation of the combustion front inside the core.

The average velocity of the combustion front for Test 11 was calculated as 0.16 m/h which is almost half the velocity in Test 10, where water was present (Appendix C). Since the injection flux for both tests was the same, this implies a higher air requirement for Test 11 (no water). Also the average temperature rise in Test 11 was 114 °C. This is almost double the average temperature rise in the tests that include interstitial water. The high air requirement and the high average peak temperatures (i.e. high average heat generation) reflect the higher fuel load in Test 11. The presence of steam in the vapor phase tends to make the vapor phase more fuel rich. Observations in Test 11 imply that the absence of water enables the vapor phase to remain in the flammable range. It is apparent from Figure 4-23 that the absence of water leads to a more uniform shape for the combustion zones which reflects the fact that the combustion reactions are consuming the entire available hydrocarbon. In this section, it is worth briefly reviewing the result of Test 13 that was described in detail in Chapter 4. Test 13 was a nitrogen injection test that was performed on Oil A in the absence of interstitial water: no

evaporation front could be observed in this test. This indicates that interstitial water plays a significant role in the development of a visible evaporation front. Also, no evaporation front is apparent from the temperature profiles of air Test 11 which did not include interstitial water (Figure 4-23).

5.4 Effect of Oil Composition on Oxidation/Combustion Behavior in HPRT Tests

Figure 5-13 compares the velocity of the evaporation fronts in nitrogen injection Test 12 that was performed on $n\text{-C}_{15}\text{H}_{32}$ and with that for Test 1 (high flux nitrogen injection test performed on Oil A). The velocity of propagation through Zones 2 and 3, and Zones 3 and 4 are determined separately from the last three zones (Zones 5, 6, and 7). There is a distinct increase in the evaporation fronts' velocity as the fronts pass through Zone 4 to Zone 5.

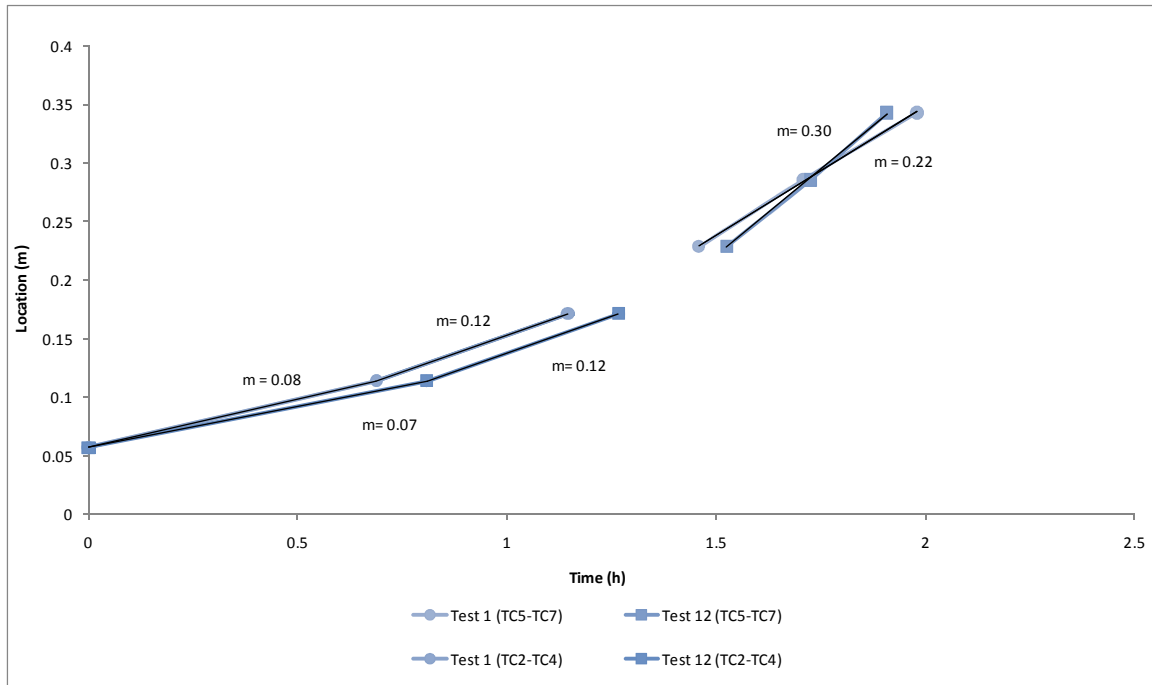


Figure 5-13: Evaporation front locations for Test 1 (Oil A, nitrogen, $38.22 \text{ sm}^3/\text{m}^2\text{h}$) and Test 12 ($n\text{-C}_{15}\text{H}_{32}$, nitrogen, $38.22 \text{ sm}^3/\text{m}^2\text{h}$); velocity of the evaporation front in Test 12 has been modified to follow the same temperature ramp rate as in Test1; time zero represents the onset of formation of the fronts

As Figure 5-13 shows, location of the first three zones displays similar velocities for the evaporation fronts in Tests 1 and 12 in spite of the differences in the hydrocarbon composition. The velocities of the fronts become different when passing through the last three zones. This indicates that at lower temperatures, the evaporation front velocity is dictated by the water phase in the early portion of the tests but is then sensitive to the oil composition over the later portion.

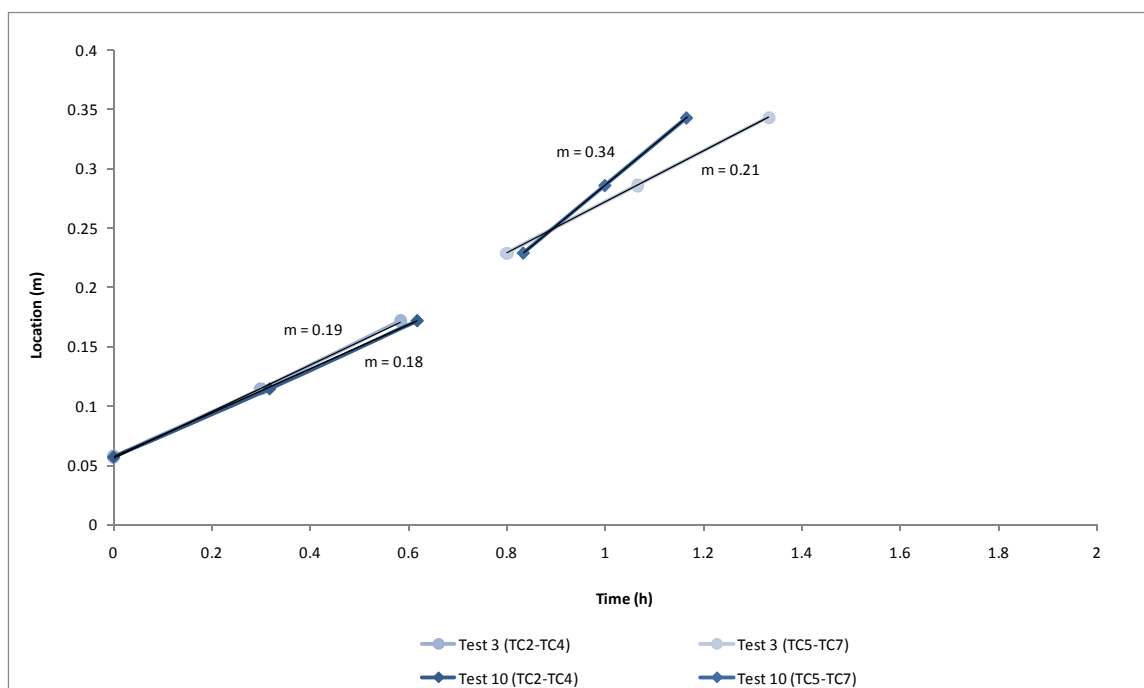


Figure 5-14: Oxidation/combustion front locations for Test 3 (Oil A, air, $38.22 \text{ sm}^3/\text{m}^2\text{h}$) and Test 10 ($n\text{-C}_{15}\text{H}_{32}$, air, $38.22 \text{ sm}^3/\text{m}^2\text{h}$)

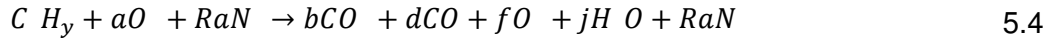
Figure 5-14 provides a comparison of the velocity of the combustion fronts for the two high flux air injection tests on Oil A (Test 3) and on $n\text{-C}_{15}\text{H}_{32}$ (Test 10). Similar to the behavior observed for the evaporation fronts for the nitrogen injection tests shown in Figure 5-13, the combustion fronts display slightly different velocities over the last three zones, reflecting different phase behaviors for Oil A and $n\text{-C}_{15}\text{H}_{32}$. The similarity in the front velocities and temperature histories supports the selection of the pure paraffin $n\text{-C}_{15}\text{H}_{32}$ as a representative single component for the paraffinic Oil A.

5.5 Analysis of Gas Phase Parameters

In this section, the product gas compositions of the air injection tests are analyzed. Also the combustion “gas phase parameters” and the trend over which they tend to vary during an air injection test are employed to study the vapor phase oxidation/combustion

behavior along with the path of the reaction kinetics. Some of the parameters that are discussed in this section are apparent atomic ratio of hydrogen to carbon (H/C), molar ratio of carbon monoxide to carbon dioxide (CO/CO₂), fractional conversion of reacted oxygen to carbon oxides, injected-air to fuel ratio in sm³/kg, and reacted-air to fuel ratio in sm³/kg. The gas phase parameters are solely based on the CO, CO₂, O₂, and N₂ concentrations in the product gas; hence, the parameters are not independent.

If the high temperature combustion reaction is described by the following basic equation:



where $R = \left(\frac{y_{N_2}}{y_{O_2}} \right)_{Feed\ Gas}$; then combustion gas parameters can be calculated as follows:

$$\text{Apparent atomic H/C ratio} = \frac{4 \left(\frac{[N_2]}{R} [CO_2] + \frac{[CO]}{2} [O_2] \right)}{([CO_2] + [CO])} \quad 5.5$$

$$\text{Fractional conversion of reacted } O_2 \text{ to Carbon oxides} = \frac{([CO_2] + \frac{[CO]}{2})}{\frac{[N_2]}{R} [O_2]} \quad 5.6$$

$$\text{Injected-air/fuel ratio} = \frac{3.64(1 + \frac{[N_2]}{R})}{12.011([CO_2] + [CO]) + 4.032 \left(\frac{[N_2]}{R} [CO_2] + \frac{[CO]}{2} [O_2] \right)} \quad 5.7$$

$$\text{Reacted-air/fuel ratio} = \frac{3.64(1 + \frac{[N_2]}{R}) [O_2]}{12.011([CO_2] + [CO]) + 4.032 \left(\frac{[N_2]}{R} [CO_2] + \frac{[CO]}{2} [O_2] \right)} \quad 5.8$$

The fractional oxygen/air utilization is defined as

$$\text{Fractional oxygen/air utilization} = \frac{\frac{[N_2]}{R} [O_2]}{\frac{[N_2]}{R}} \quad 5.9$$

In this chapter, the [] signifies normalized composition in mole percent. For all of the HPRTTO tests, the first few GC samples were affected by the helium that was being displaced out of the system and consequently the early time GC readings were of low precision. Therefore, the first product gas composition and gas phase parameters data points are not reported in the figures associated with the gas phase parameters.

In Figure 4-5 for Test 2 (Oil A, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$) in Chapter 4, it was noted that the concentration of oxygen in the gas phase began to drop slowly at around 150°C prior to the formation of the first exothermic reaction zone (indicated by TC2) at 180°C . The initial slow reduction in oxygen concentration reflects the initiation of the oxygen addition reactions. The oxygen utilization during the propagation of the vapor phase reaction zone was essentially complete. However, the slow build up of oxygen concentration in the gas phase after oxygen breakthrough suggests that the reaction zone leaves residue in the core which later is consumed by oxygen at a slow reaction rate.

The interesting feature about the nitrogen concentration history is its increase in response to the initiation of the oxygen addition reactions. The increase in nitrogen concentration suggests that the uptake of oxygen molecules from the gas phase through oxidation reactions is not associated with equal molar replacement of reaction products in the vapor phase gas molecules. This may indicate that either the oxygen is consumed by the oxygen addition reactions or it is reacting with hydrogen through bond scission reactions to form liquid water. It is believed that both bond scission and oxygen addition reactions may occur below 300°C , so there is most likely a competition between these two types of reaction at these temperature conditions. However, the nitrogen concentration tends to drop during the propagation of the reaction zone, when bond scission reactions become more dominant at higher temperatures. Nitrogen

concentration continues to drop after oxygen breakthrough when the combustion of the residue results in less water production.

Figure 5-15 presents a plot of $(\text{CO}_2+\text{CO})/\text{N}_2$ and CO/CO_2 ratios with respect to the temperature profile in Test 2. The CO/CO_2 ratio highlights the variations in composition of the carbon oxides during the test. This ratio increased (from zero) as a response to initiation of the oxygen addition reactions at around 150 °C, remained almost constant during the propagation of the reaction wave and then decreased over the remainder of the test. This indicates that production of CO_2 is favored over CO during the combustion of the residual hydrocarbon remaining after passage of the reaction wave. The plot of $(\text{CO}_2+\text{CO})/\text{N}_2$ indicates an average value of 0.15 for the combustion of Oil A. The typical value observed during combustion tube tests of heavy oils for this ratio is around 0.21.

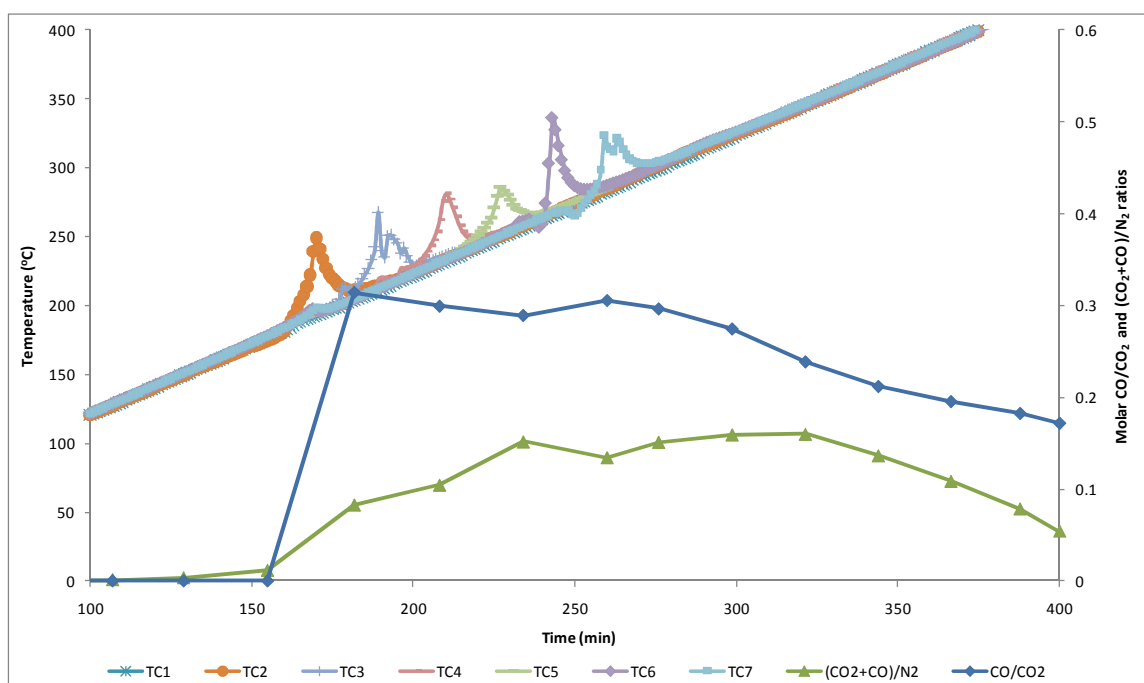


Figure 5-15: Molar CO/CO_2 and $(\text{CO}_2+\text{CO})/\text{N}_2$ ratios along with the temperature history for air injection Test 2 (Oil A)

The apparent atomic H/C ratio for Test 2 is shown in Figure 5-16. Apparent H/C ratio assumes that the oxygen removed from the gas phase is only utilized by the combustion reactions to form carbon oxides and water. Therefore, it does not account for the removal of oxygen by the oxygen addition reactions. High H/C values seen in Figure 5-16, prior to formation of the distinct reaction zone, reflect the oxygen addition reactions with production of very low amounts of carbon oxides. On initiation of the combustion reactions, the H/C ratio drops sharply to a value of 5.1 and then decreases following a near linear trend up to the time of oxygen breakthrough. It is observed that there is a discontinuity around 250 °C which suggests a change in the kinetics path of the reactions. The H/C ratio stabilizes around a value of 1.5 during the combustion of the residue. The H/C trends observed for Test 2 were also identified for the rest of air injection tests. Figures can be found in Appendix D. These figures also feature the plot of $(\text{CO}+\text{CO}_2)/\text{N}_2$ along with the H/C ratio and temperature history.

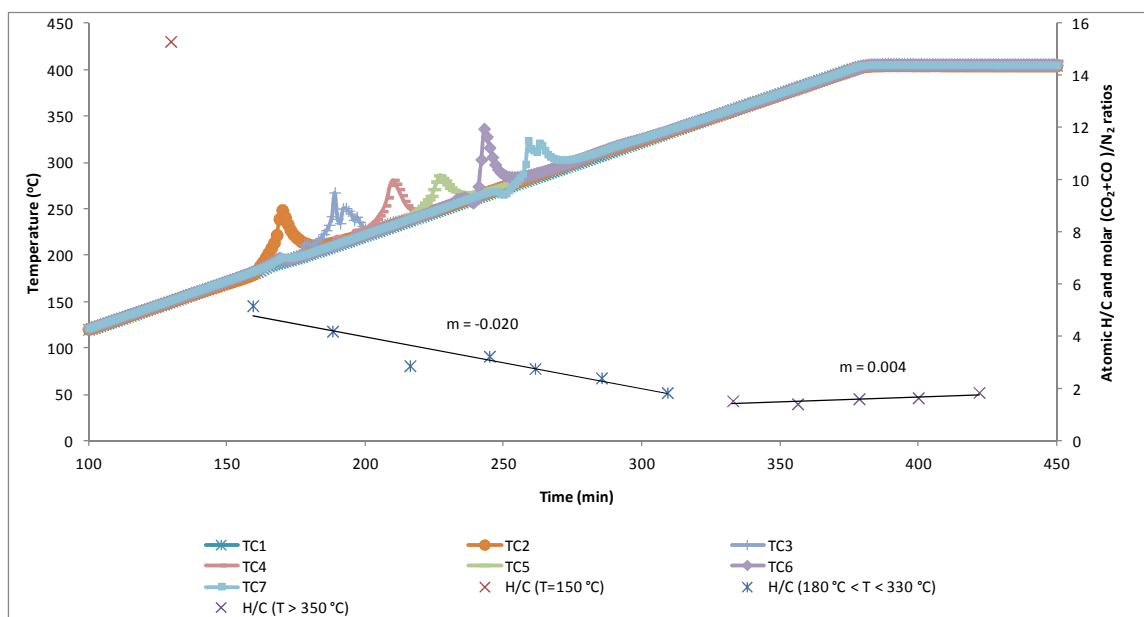


Figure 5-16: Apparent atomic H/C ratio along with the temperature history for high flux air injection Test 2 (Oil A)

The low H/C ratio after oxygen breakthrough indicates that the combustion fuel leans towards the heavier hydrocarbon molecules with less hydrogen atoms (aromatic type fuel), hence less water is produced. The levels of apparent H/C ratios during the time that the reaction wave propagated through the core are higher than is expected for the combustion of a hydrocarbon. Therefore, the combustion reactions must either be competing with oxygen addition reactions or consuming generated hydrogen or both. The H/C ratio during the first zone in high flux Test 2 is almost half the H/C at the first zone in low flux Test 6 (Figure 5-17). This indicates the higher extent of oxygen addition reactions in low flux tests, due to the composition of the vapor mixture falling on the rich side of the flammability limit.

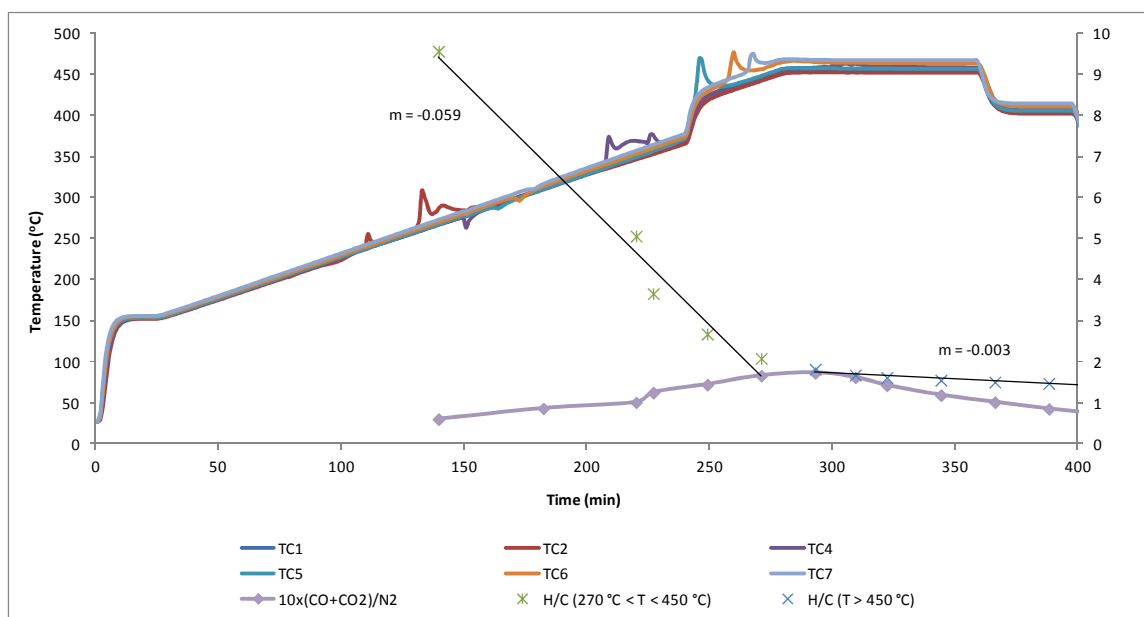


Figure 5-17 Apparent atomic H/C ratio along with the temperature history for low flux air injection Test 6 (Oil A)

In Figure 5-18 a plot of fractional conversion of oxygen to carbon oxides against the apparent atomic H/C ratio for Test 2 is presented. The behavior of apparent atomic H/C ratio was discussed above; however, fractional conversion of oxygen to carbon oxides ratio provides a more direct indication of the fate of the reacted oxygen. High levels of fractional oxygen conversion correspond to low apparent H/C ratios while low levels of the fractional conversion (high apparent H/C) generally signify the consumption of oxygen by oxygen addition reactions.

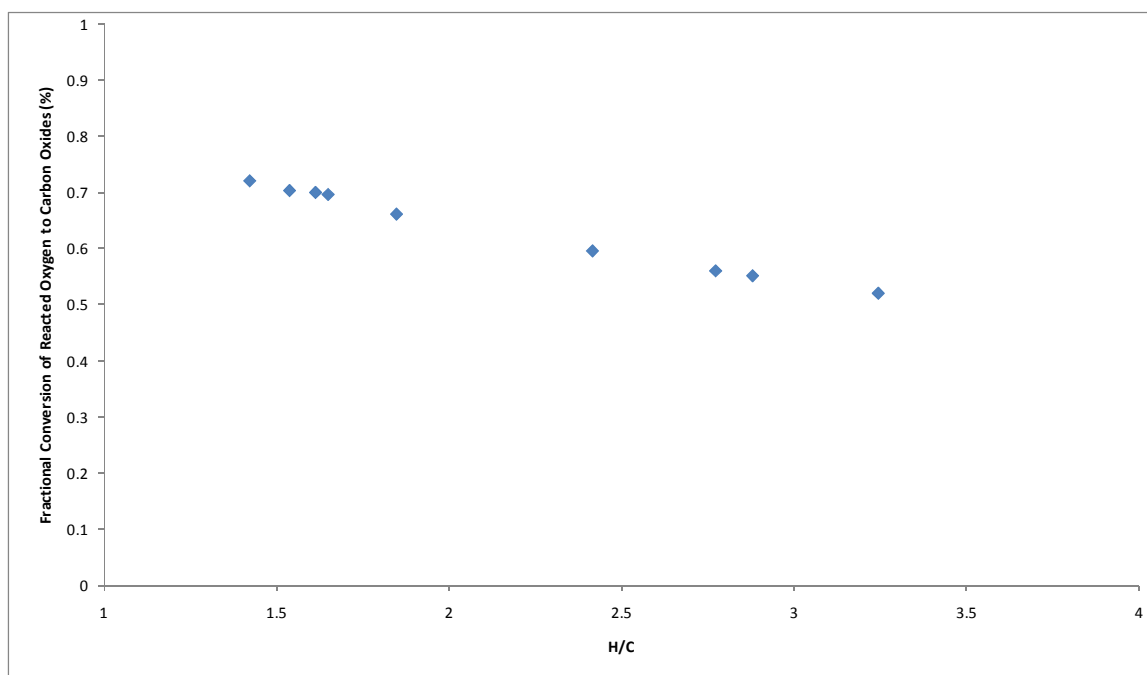


Figure 5-18: Fractional conversion of oxygen to carbon oxides with respect to the apparent atomic H/C ratio for air injection Test 2 (Oil A)

Appendix D provides plots of oxygen utilization with respect to the temperature history of the air injection tests. In addition to oxygen utilization curves, the amount of oxygen uptake per 100g of initial oil (mol/g) is shown in the same plot. Millour *et al.* (1987) found that in order for coke to form in the air injection tests, the total oxygen uptake by the time of coke formation should be at least 4 grams per 100 grams of initial oil. The oxygen uptake curves in this appendix show that in HPRT0 tests the onset of coke formation is early in the test at low temperatures. This finding helped to tune the reactions during the numerical modeling of this study (reported in Chapter 7).

It was described in Section 5.2.1 that air/fuel ratio in conventional gas phase combustion literature determines if the composition of a mixture of air and fuel falls in the flammability envelop of that mixture. The “stoichiometric” air/fuel ratio is the amount of

air required for complete combustion of the fuel to carbon dioxide and water. If the air/fuel ratio of a mixture is greater than the stoichiometric air/fuel ratio, the mixture is fuel-lean and accordingly a fuel-rich mixture has an air/fuel ratio smaller than stoichiometric air/fuel ratio. A rule of thumb number for air/fuel ratio of stable burning oil, undergoing complete oxygen utilization, during in situ combustion is $10.8 \text{ m}^3/\text{kg}$ of fuel. Since during in situ combustion tests the oxygen utilization may be less than 100%, both injected-air/fuel and reacted-air/fuel ratios are evaluated. These two ratios are related by the overall oxygen utilization. Figure 5-19 presents the injected-air/fuel and reacted-air/fuel ratios, with respect to the temperature history for Test 2.

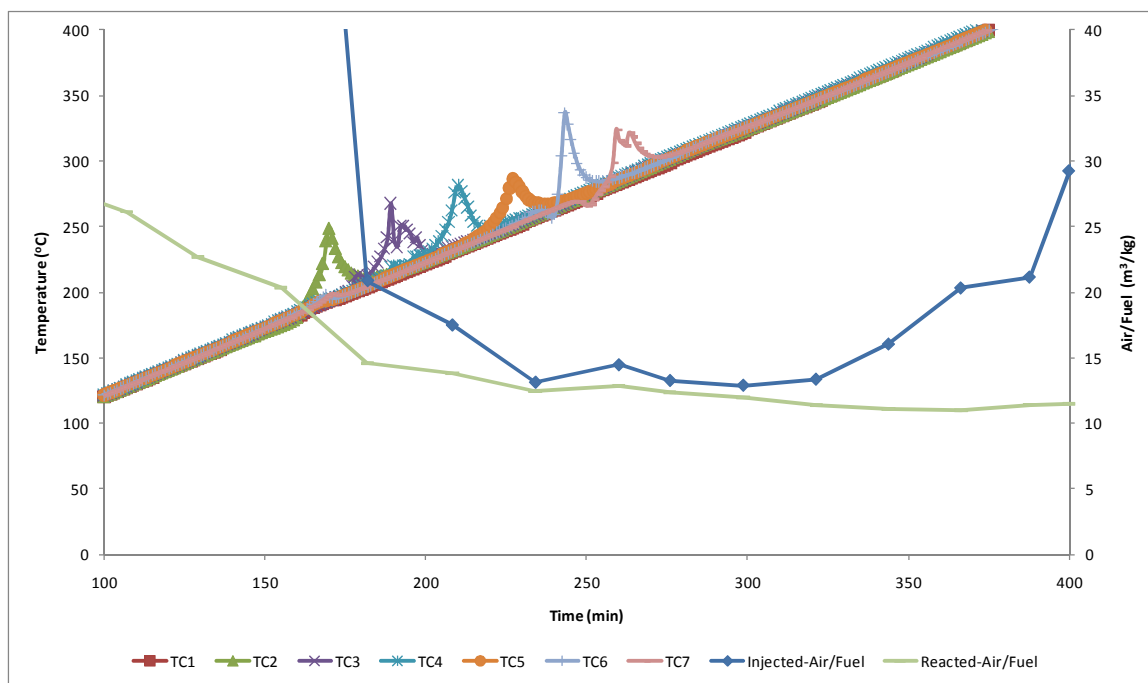


Figure 5-19: Injected-air/fuel and reacted-air/fuel ratios along with the temperature history for air injection Test 2 (Oil A)

In Figure 5-19 the temperature of TC6 reflects a change in the kinetics which is seen from the increased slope of the leading edge and the sharpness of its exothermic peak. Since the global reaction rate at this location is limited by the rate of delivery of oxygen under the constant air injection flux of this test, the sharp and narrow peak can indicate an increase in the oxygen reaction rate which enables the oxygen to be consumed in a smaller axial length of the core. Figure 5.19 shows a 12.6 (sm³/kg) reacted-air/fuel ratio at 250 °C, which indicates near stoichiometric conditions in the vapor phase for Test 2. The shape of the exothermic peak seen from TC 7 suggests that the vapor phase burn is exhausting. This suggests that the vapor phase is approaching a fuel rich limit and falls out of the flammable range as the oxygen starts to break through. According to Figure 5-11, at high pressures (like that of HPRT0 tests) right in the range that the stoichiometric composition falls towards the rich side of the flammable range, there's a possibility for explosion of the cool flame. The sharp peak at Zone 6, where composition of the vapor phase according to Figure 5-19 is approaching the rich limit can be indicative of a cool flame ignition.

After the reaction zone has propagated through the reactor, the injected-air/fuel ratio increases while the reacted-air/fuel ratio shows a declining trend over the duration of the test. From the oxygen break through time till the end of the test, the very slow build up of oxygen composition signifies the presence of a residual hydrocarbon remaining in the core. The residue reacts slowly with oxygen and produces carbon oxides. The fact that the coke-like residual hydrocarbon burns slowly has been emphasized in this chapter and will be pointed out in Chapter 7 also. This is in order to highlight the point that HPAI reactions cannot be modeled with a classical in-situ combustion coke-burn reaction. The slow rate of oxygen uptake suggests that the heterogeneous reactions are diffusion-controlled at this point. This means that the high injected-air/fuel ratio in Figure 5-19,

after oxygen break through, should not be interpreted as indication of a fuel lean condition since the reactions are not happening in the vapor phase.

Prior to the formation of the exothermic front at Zone 2, high reacted-air/fuel ratios are observed (Figure 5-19). As mentioned previously, this is due to the oxygen addition reactions which remove the oxygen from the gas phase but do not produce significant carbon oxides. Oxygen addition reactions are traditionally associated with the liquid phase. However, the nitrogen injection Test 1 has shown the evaporation front to form at 150 °C. Therefore, it is possible that the oxygen addition reactions may also occur in the vapor phase.

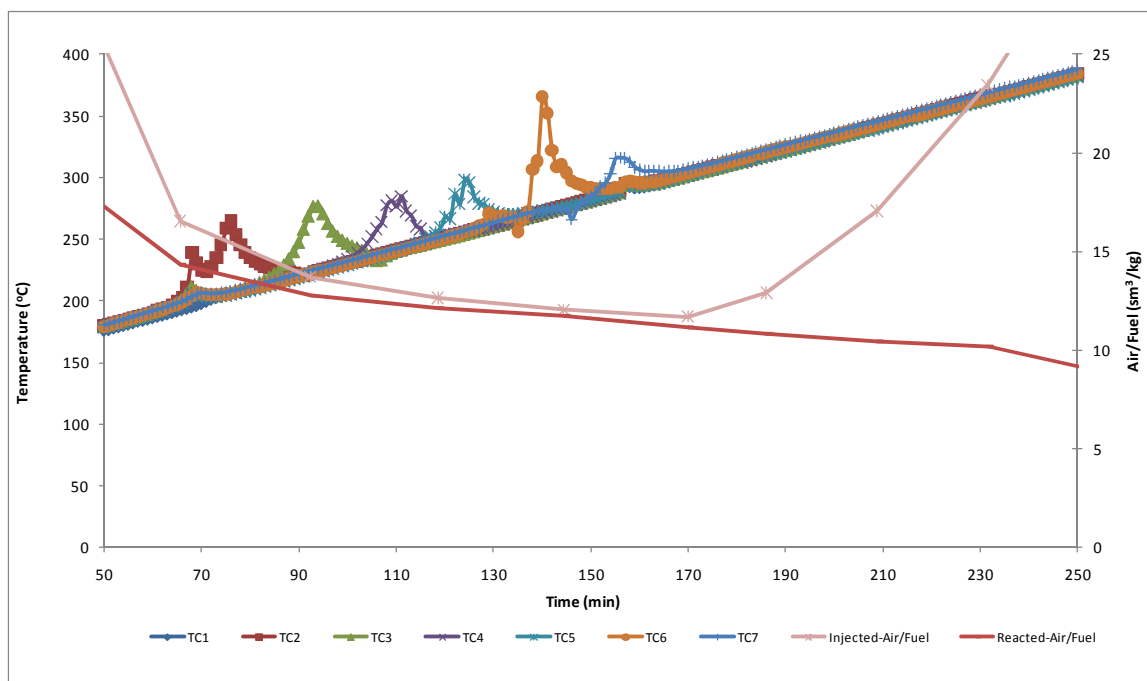


Figure 5-20: Injected air/fuel and reacted-air/fuel ratios for air injection Test 3 (Oil A)

The product gas composition trends obtained from air injection Test 3 (under the same conditions as Test 2 but with preheating of the core to 150 °C prior to air injection) are very similar to those of Test 2 (Figure 4-8). The reacted air/fuel ratio for Test 3 is presented in Figure 5.20. Both tests show very similar reacted-air/fuel ratios just prior to the appearance of the reaction zone at TC 2. As stated previously, oxygen addition reactions dominate prior to appearance of the gas phase combustion wave.

The product gas compositions of air injection Test 10 were illustrated in Figure 4-22. Test 10 was performed on the pure hydrocarbon ($n\text{-C}_{15}\text{H}_{32}$) under the same conditions as Test 3. Similar gas composition trends to Test 2 and Test 3 were observed during Test 10. Although Test 10 was performed on pure $n\text{-C}_{15}\text{H}_{32}$, the presence of residual fuel in the core after the passage of the exothermic front is evident by the slow build up of oxygen in the gas phase following passage of the vapor phase combustion zone. As will be described in the following section (5.6) generation of new heavier molecules through oxidation/cracking reactions was confirmed later by the simulated distillation analysis performed on the produced oil. The set point temperature for Test 3 was 300°C which was lower than that used for other air injection tests; however, the residual hydrocarbon underwent combustion at this temperature.

Figure 5-21 depicts the injected-air/ fuel and reacted-air/fuel ratios for Test 10 with respect to its temperature history. From the time that gas composition data were first available until the combustion zone had traversed the core, the oxygen utilization was complete; hence the injected-air/fuel and reacted-air/fuel are identical. However, when the kinetics switch into combustion of the residual the oxygen utilization drops and the injected-air/fuel ratio continues to increase for the duration of the test. The theoretical stoichiometric air/fuel ratio for pure $n\text{-C}_{15}\text{H}_{32}$ (considering the injection air composition of Test 10) is 11.07 (sm^3/kg). The temperature profile in Figure 5-21 shows that although

the slopes at the leading edges of the last two exothermic peaks are identical, the last zone displays a higher temperature rise. This is associated with an injected-air/fuel ratio of 11.74 (sm^3/kg), i.e. stoichiometric condition.

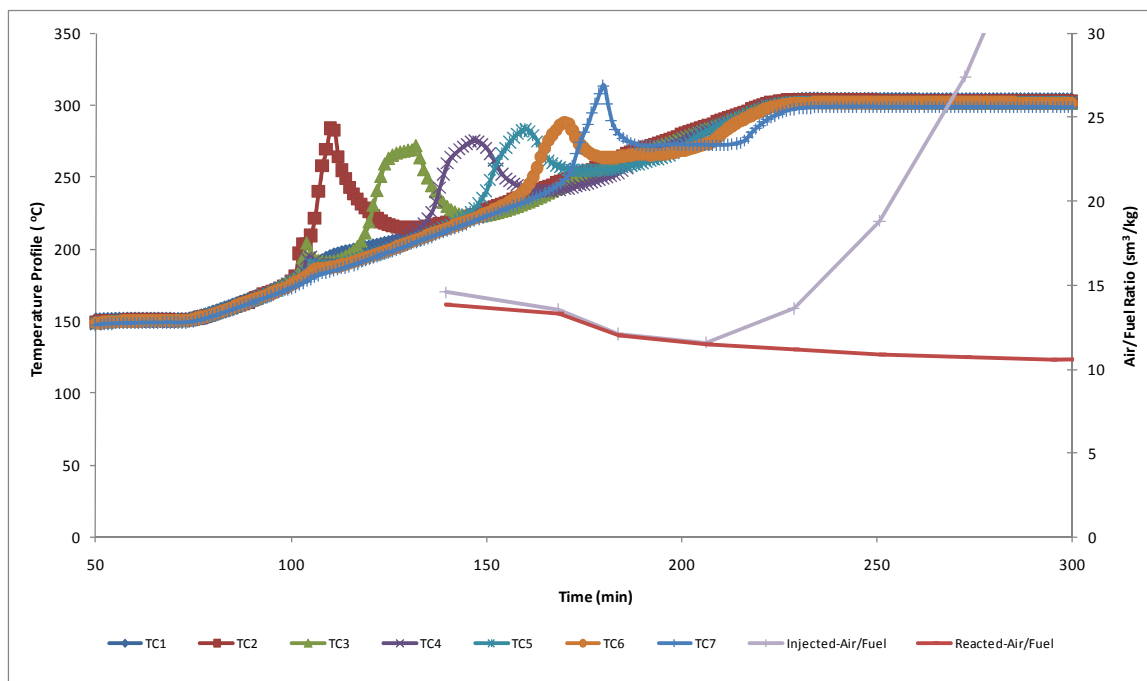


Figure 5-21: Injected air/fuel and reacted-air/fuel ratios for air injection Test 10 ($\text{n-C}_{15}\text{H}_{32}$)

Test 11 is an air injection test performed on $\text{n-C}_{15}\text{H}_{32}$ (at the same operating conditions as of Test 10) but with zero connate water saturation. Figure 4-23 presented the product gas compositions as observed for Test 11 with respect to the temperature history. Unlike the gas composition trends observed for air injection tests which included connate water, product gas compositions for Test 11 remained essentially constant during propagation of the exothermic wave. This test showed an almost constant near stoichiometric injected-air/fuel ratio (Figure 5-22) prior to oxygen breakthrough. After oxygen broke

through, there was a more rapid oxygen build up in the product gas stream (Figure 4-23), compared to that of the tests which included connate water. This indicates that the amount of solid residue left on the core in the absence of water is much less than when water is present; and it suggests that water alters the kinetics of the combustion reactions due to its dilution effects in the vapor phase. The uniform combustion behavior observed in absence of water in this test emphasizes that the temperature profiles and product gas composition parameters observed during an HPAI process are dependent on the presence of connate water.

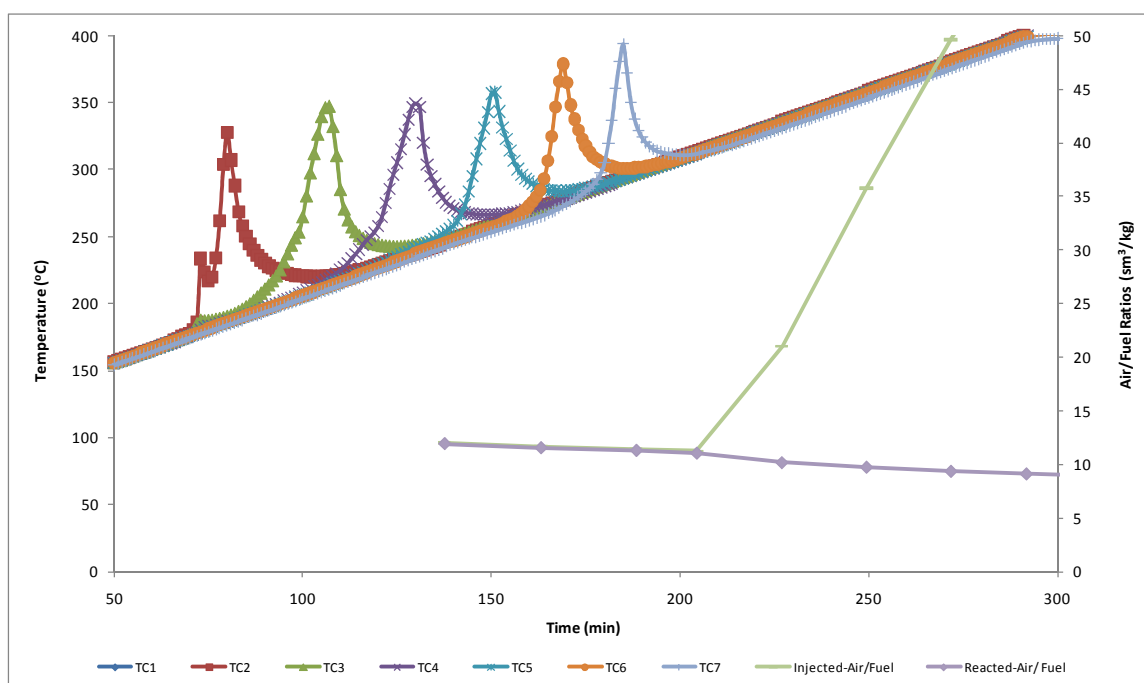


Figure 5-22: Injected-air/fuel and reacted-air/fuel ratios for air injection Test 11 (n- $C_{15}H_{32}$, no connate water)

5.6 Analysis of the Simulated Distillation Results

In this section, results of the simulated distillation analysis performed on the produced liquid oil of air injection Test 1, Test 10, and nitrogen injection Test 12 and Test 13 are presented and compared. The complete results of simulated distillation analysis for all tests are provided in Appendix B. Figure 5-23 compares the total liquid recovery of the individual carbon number groups between nitrogen injection Test 1 and Test 13 involving Oil A. Since the composition of individual carbon number groups in original Oil A and produced oil are available through simulated distillation analysis of these oils, the recovery (wt%) of each carbon number group can be calculated based on these compositions, accounting for the total initial mass of Oil A in the core and total mass of liquid oil produced. Both Test 1 and Test 13 were conducted at the same conditions; however, Test 13 excluded connate water. Lower recoveries for the light end portion in Test 1 are due to the procedure employed to collect the liquid samples for the first few HPRTTO tests. Some of the water and light ends were lost as vapor and/or liquid droplets as the individual liquid samples were drained from the high pressure trap. However, the higher recovery of the heavy end portion in Test 1 is due to “steam distillation” (Duerksen and Hsueh 1983). The evaporation mechanism in Test 1 benefits from the vapor pressure of the connate water which adds to the partial pressure of the hydrocarbons (Wu and Fulton, 1971) and enables much higher (1.5-3 times more) recoveries of the heavier hydrocarbon molecules. The difference between the recoveries of the individual fractions in the two tests rises as the carbon numbers increase.

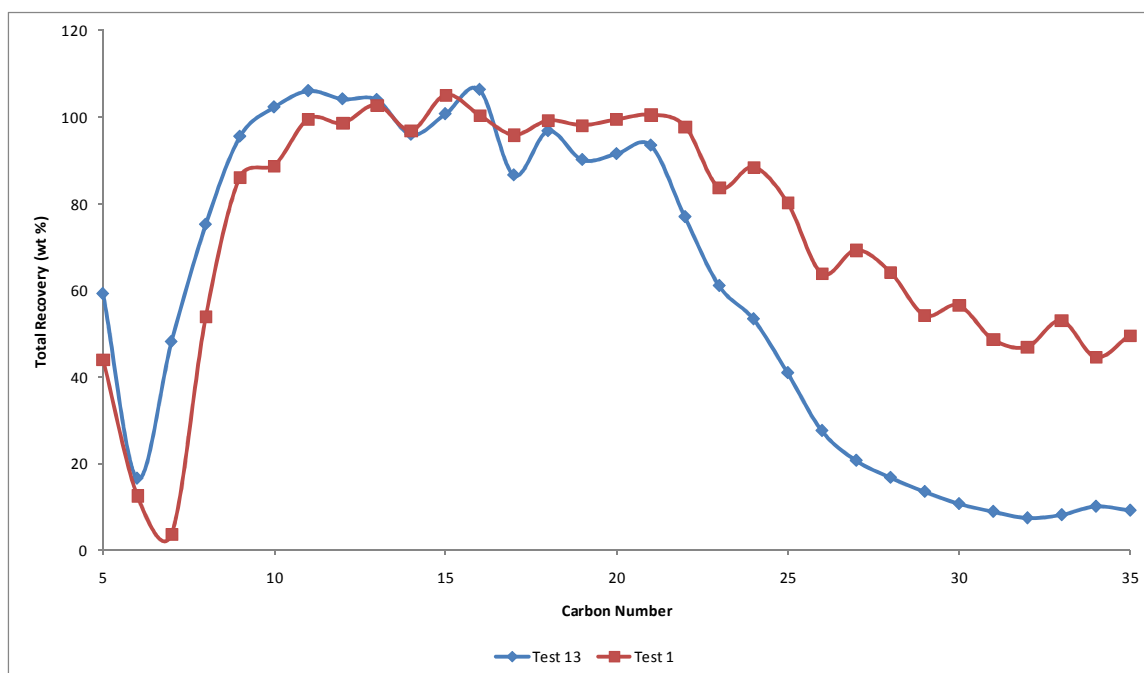


Figure 5-23: Simulated distillation analysis of the produced oil from nitrogen injection Test 1 (Oil A) and nitrogen injection Test 13 (Oil A, no connate water): total recovery (wt %) of each carbon number group

Simulated distillation analysis of the produced oil for air injection Test 10, conducted on pure $n\text{-C}_{15}\text{H}_{32}$, showed that only 80% of the product oil was the original $n\text{-C}_{15}\text{H}_{32}$ and the rest was distributed over a range of light to heavy hydrocarbons (Appendix B, Figure B-10). This is an important observation, highlighting how cracking reactions (both thermal and oxygen induced) can extensively alter the original fuel in air injection tests. Figure 5-24, in a logarithmic scale, compares the composition of hydrocarbon groups in produced oils in air injection Test 10 and nitrogen injection Test 12 both involving $n\text{-C}_{15}\text{H}_{32}$. The produced hydrocarbon from nitrogen injection Test 12 contained 15% non-original fractions due to thermal cracking of $n\text{-C}_{15}\text{H}_{32}$. On the other hand, hydrocarbons produced during the air injection Test 10 included 20% non-original fractions. This illustrates how the “oxygen induced cracking” reactions, in addition to thermal crackings contribute to

modification of the fuel and consequently alter the kinetics of oxidation/combustion reactions.

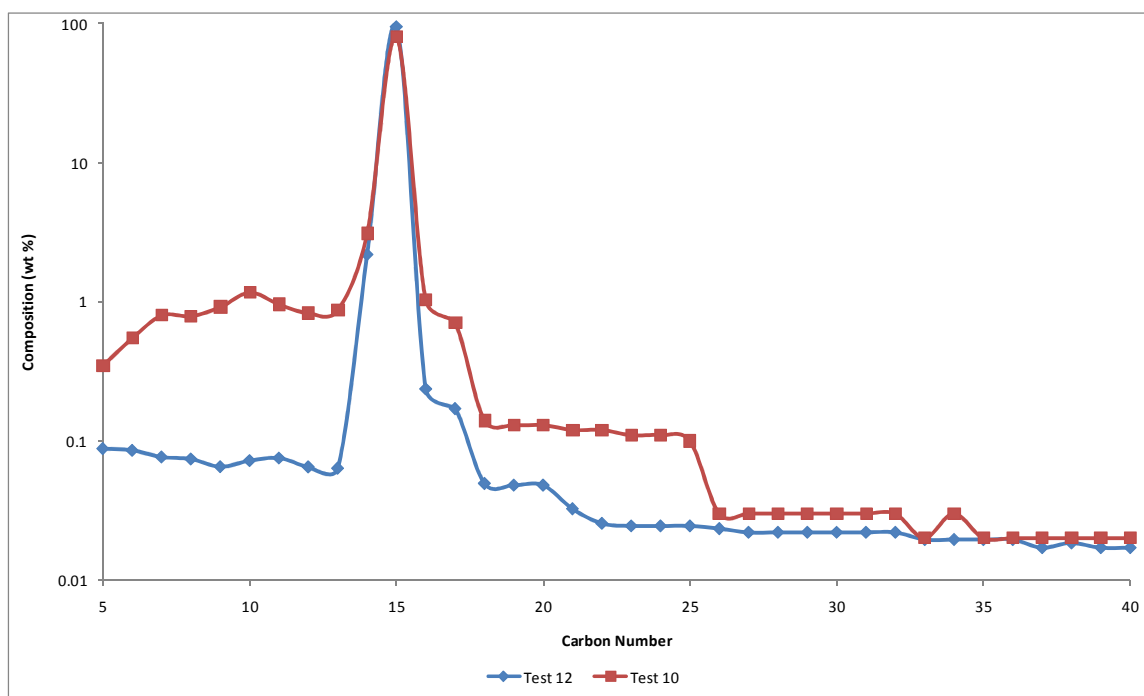


Figure 5-24: Simulated distillation analysis of the produced oil from air injection Test 10 ($n\text{-C}_{15}\text{H}_{32}$) and nitrogen injection Test 12 ($n\text{-C}_{15}\text{H}_{32}$): Composition (wt %) of each carbon number group in the produced oil sample in logarithmic scale

Figure 5-25 presents the simulated distillation analysis for produced oil of nitrogen injection Test 13 (Oil A, no connate water) in three different samples which was enabled through the modified liquid collection system used for Tests 12-15. This graph shows that the majority of $\text{C}_5\text{-C}_{10}$ fraction is produced in Trap 1 (before 300 °C), while most of the $\text{C}_{11}\text{-C}_{17}$ fraction is produced in Trap 2 which corresponds to the temperature range between 300 °C and 400 °C. The heavier molecules (C_{18}^+) are mostly produced during the depressurization stage of the test.

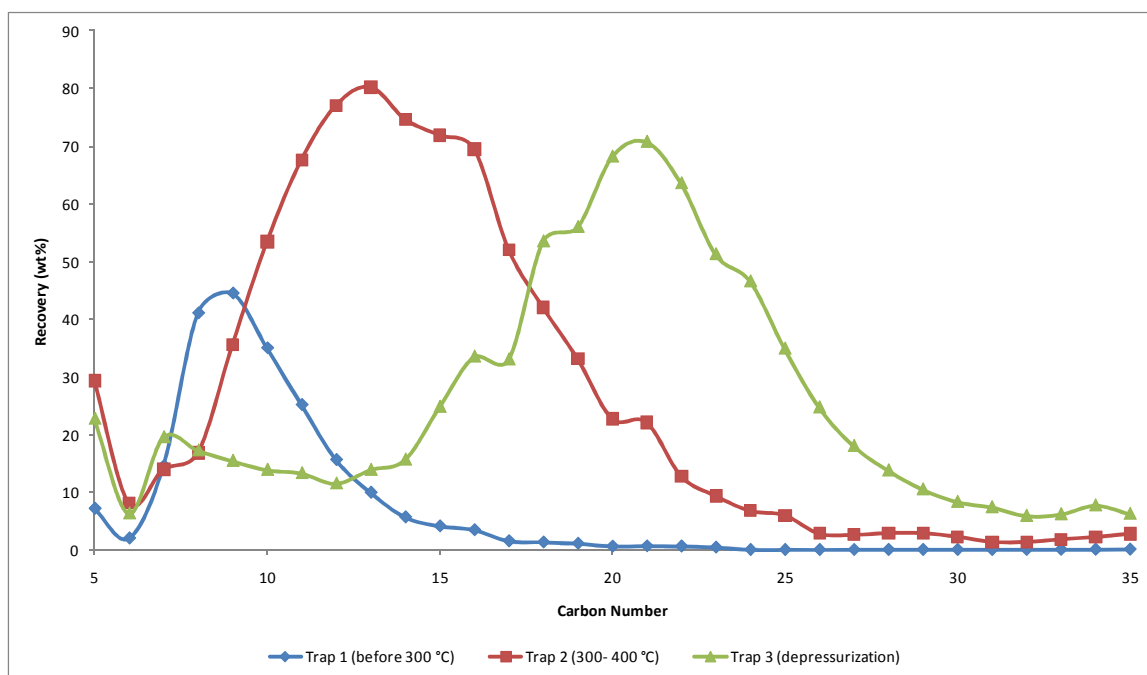


Figure 5-25: Simulated distillation analysis of the produced oil from nitrogen injection Test 13 (Oil A, no connate water), during three different temperature ranges: recovery (wt %) of each carbon number group

Chapter Six: Equation of State Fluid Characterization and Numerical Phase Behavior Model

As was discussed in Chapter 5, the concentration of hydrocarbon available as fuel in the vapor phase is a key factor concerning activation, progression and quality of vapor phase combustion reactions. Therefore, a meaningful combustion model requires a comprehensive, precise phase behavior model by which the fluids' compositions and characteristics are predicted most accurately. An equation of state (EOS)-based fluid property simulator (WinProp) by Computer Modeling Group (CMG) was used for phase behavior predictions. For compositional modeling, WinProp simulation package features an EOS-based formulation, where composition of the vapor phase at different temperatures can be a function of pressure, temperature, composition of the feed, and temperature-dependant composition of an optional key component. But WinProp does not enable building of a fully-compositional phase behavior model which accounts for the composition of all of the components in K-value calculations. In this study, a new methodology is developed to calculate accurate compositional K-values for thermal simulators which can generate gas-liquid component K-values at any temperature incorporating the composition of the oil in place at that particular temperature. It will be shown that the K-values generated by this methodology enhance the predictions of the phase behavior and consequently the numerical kinetics model.

6.1 Phase behavior model

In order to build a phase behavior model for Oil A, a PVT analysis performed on a recombined sample of oil and synthetic separator gas was used. The fluid properties of recombined Oil A at reservoir condition are presented in Table 3.1. The PVT analysis included a constant composition expansion (CCE) test at reservoir temperature, a five step differential liberation (DL) test at reservoir temperature from the bubble point

pressure, and a two-stage separator test. Then a phase behavior model was built for live Oil A, employing the Winprop software, based on seven oil pseudo components (Table 6.1), N_2 and CO_2 . Using the WinProp lumping scheme, C_1 to C_{30}^+ were lumped into seven pseudo components. Specific gravities were calculated from the correlation of Twu and critical properties and acentric factors were obtained from the Lee-Kesler correlation (Computer Modeling Group, 2009). Designing of the lumping scheme was based on carbon number distribution of oxidized samples of a selected light oil (Jia, 2007) in a previous study performed by the *In-Situ* Combustion Group at the University of Calgary. The Peng Robinson equation of state (Peng & Robinson, 1976) model was tuned in WinProp to the experimental data from the PVT experiments by performing a non-linear regression on gas-oil ratio, relative oil volume, gas compressibility factor, gas FVF, oil specific gravity, gas specific gravity, and oil density.

Table 6-1: Pseudo components and their compositions in live Oil A phase behavior model

Pseudo Component	Composition (mole %)
C_1	36.03
C_2 - C_5	8.54
C_6	2.60
C_7 - C_9	12.36
C_{10} - C_{14}	17.10
C_{15} - C_{20}	10.94
C_{21} - C_{27}	6.32
C_{28} - C_{29}	1.52
C_{30}^+	3.73

For the purpose of tuning, critical properties of the lightest (C_1) and heavier (C_{21-27} , C_{28-29} , and C_{30}^+) components in the scheme were allowed to be refined as regression parameters. Binary interaction coefficients and volume shifts were also tried; however reasonable results were obtained excluding the latter parameters. Viscosity was calculated using Jossi-Stiel-Thodos correlation as described in the WinProp user's manual. A comparison between the PVT tests' experimental data and the EOS calculated properties is presented in Table 6.2 and Figures 6-1 to 6-4.

Table 6-2: Comparison of the experimental and EOS calculated properties for live Oil A

Property	Experimental Data	EOS Calculated Data Before Regression	EOS Calculated Data After Regression	Error (%)
Saturation Pressure (MPa)	15.60	15.86	16.20	4
Gas Oil Ratio @ 15.6 MPa (m^3/m^3)	77.00	82.85	84.20	9
Formation Volume Factor	1.34	1.33	1.33	0.75
API Gravity	37.00	42.32	39.59	7

Since the oil used for HPRT0 tests is a dead oil, the fine tuned live oil A model was flashed to room temperature in order to find the composition of the dead oil for further use in the numerical simulation of nitrogen and air injection models. The number of liquid oil pseudo components was consequently reduced to 7, having evaporated C_1 and C_2 - C_5 components.

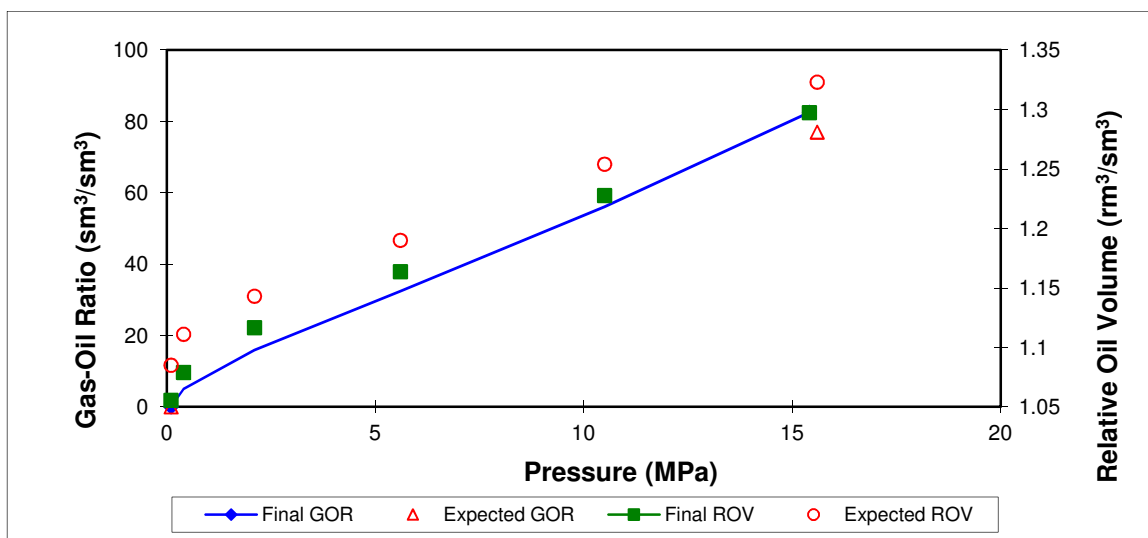


Figure 6-1: Experimental (differential liberation test) and tuned values for gas-oil ratio and relative oil volume; Oil A

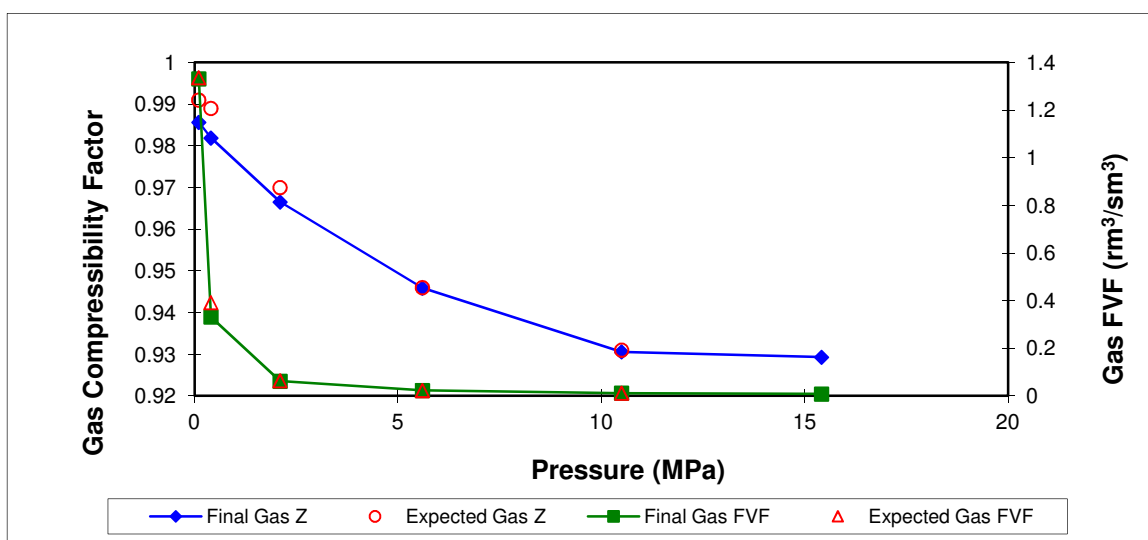


Figure 6-2: Experimental (differential liberation test) and tuned values for gas compressibility factor and gas FVF; Oil A

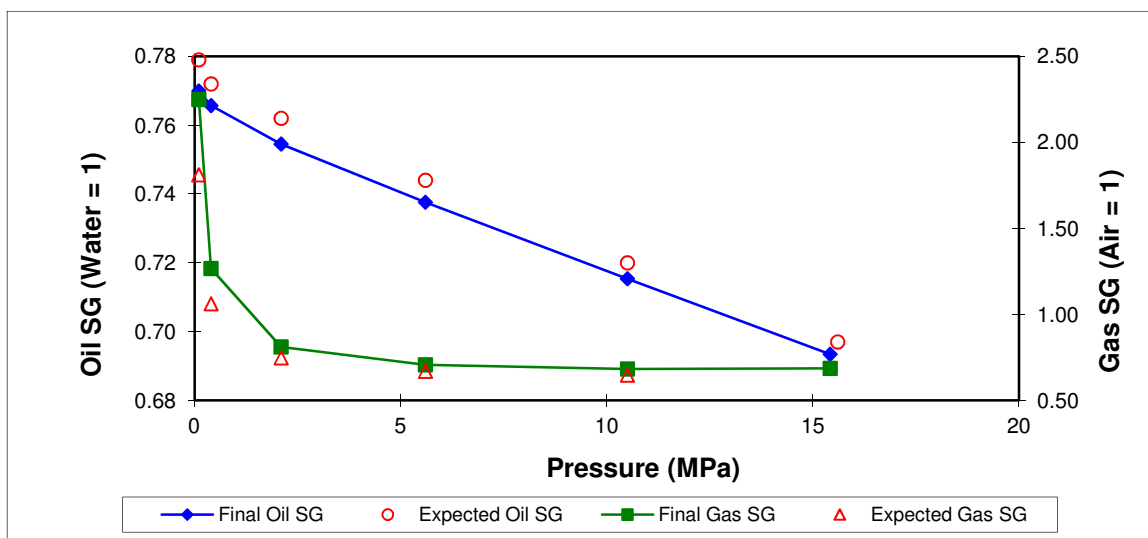


Figure 6-3: Experimental (differential liberation test) and tuned values for oil and gas specific gravity; Oil A

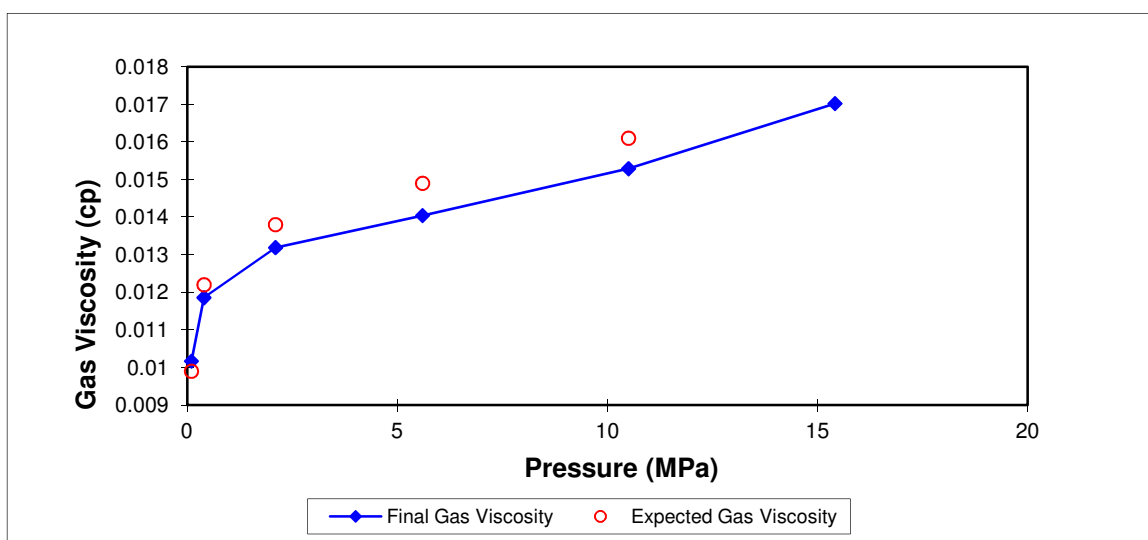


Figure 6-4: Experimental (constant composition expansion test) and tuned values for gas viscosity; Oil A

6.2 Compositional equilibrium K-values

A multi-phase compositional study was conducted on the mixture of Oil A/water/nitrogen with initial compositions identical to the conditions of the HPRTTO tests. In order to obtain primary understanding of the vaporization phenomenon inside the HPRTTO reactor, a basic hypothetical model consisting of several flash drums all at the same pressure (13.6 MPa) but, at various increasing temperature steps was constructed. At each temperature step a three-phase flash was performed on the liquid feed and K-values were calculated. The generated vapor was removed (to simulate the evaporated components being swept away by the flowing air inside the reactor) and the remaining liquid was transferred into the next cell. A constant number of moles of nitrogen (based on the tests' fixed injection flux) were fed to the next cell. Each temperature step was 30 °C higher than the previous step. This was chosen, based on a time average of 30 minutes for the gas to traverse the whole reactor under HPRTTO tests' conditions, considering the 60 °C/h defined rate of heating for the reactor.

It was reviewed in detail in Chapter 2 that accuracy of the phase behavior model for a proper simulation of a light oil air injection processes is a key factor. It was also described how fully-compositional K-values can perform differently than the K-values generated through correlations which only depend on pressure and temperature. It was realized in this study, that composition of the hydrocarbon in the vapor phase at any time has a direct impact on the oxidation/combustion reaction kinetics of HPAI and in order to avoid uncertainties, while conducting a kinetics study, a decent phase behavior model was essential for eliminating that uncertainty. Since the CMG STARS is not a fully compositional package, the above mentioned methodology was used to provide a table of K-values which not only were dependent on temperature and pressure, but also accounted for compositions of both vapor and liquid phases.

The parameters that affect the accuracy and applicability of K-value estimation are the temperature, pressure, composition, and degree of polarity. Therefore, selection of a proper approach is crucial to the best estimation of the equilibrium K-values. There is no need to emphasize how this sensitivity is highlighted even more for light oil mixtures. In general the widely used approaches are K-value tables, Raoult's law, the ϕ - ϕ approach and the ϕ - γ approach (Prausnitz *et al.*, 1999 and Reid *et al.*, 1987). The last two approaches are based on an EOS.

Raoult's law is based on the assumption that the vapor phase behaves like an ideal gas and the liquid phase like an ideal solution. Raoult's law is only applicable to low-pressure systems (up to about 345 kPa or 50 psia) and to systems consisting of very similar components such as benzene and toluene. This method is simple but it is inadequate when the temperature of the system is above the critical temperature of one or more of the components in the mixture. At temperatures above the critical point of a component, the vapor pressure is extrapolated, which frequently results in erroneous K-values. And this only adds to the fact that Raoult's law ignores the dependence of the K-values on composition.

One of the widely used correlations to predict K-values for computer calculations was presented by Wilson in 1968:

$$K_i = \frac{P_{ci}}{P} \exp \left[5.37(1 + \omega_i) \left(1 - \frac{T_{ci}}{T} \right) \right] \quad 6.1$$

This correlation is applicable to low and moderate pressures (up to about 3.5 MPa or 500 psia), and the K-values are assumed to be independent of composition.

In the ϕ - ϕ and ϕ - γ approach, the fugacity of each component is determined based on using an EOS. In order to calculate the fugacities and consequently the K-values, in addition to pressure and temperature the mole fractions in both phases are needed. The ϕ - ϕ approach is a powerful tool and is widely used for light hydrocarbons and non-polar systems and is reliable up to 15,000 psi (Al-Saygh *et al.*, 2004). The ϕ - γ approach is used in industry even for polar systems exhibiting highly non-ideal behavior.

CMG STARS supports K-value tables as well as correlation inputs. The correlation used by STARS was described by Equation 5.2 in the last chapter. It is solely dependent on pressure and temperature. The K-value charts also tabulate the K-values based on pressure and temperature. However, STARS features a flexibility to partially account for the compositions of a key component by allowing for three different table inputs for that component at three different compositions. Although not clearly described in the STARS manual, the basis of introducing a composition dependency for a key component roots from a study conducted by Fassihi (1992). The result of this study, which was briefly reviewed in Chapter 2, was later successfully incorporated in the West Hackberry light oil field simulation (Fassihi *et al.*, 2000).

Although STARS software enables a degree of composition dependency, the methodology suggested in this current study can help create a single K-value table at any given pressure which provides K-values at each temperature step, based on the compositions of all the components available in the vapor and liquid phase at that same step. It was mentioned that using correlation-based K-values for a sensitive process at high pressures, such as air injection in light oils ends up with improper erroneous values. The following figures are presented to highlight this matter. Figure 6-5 to Figure 6-8 compare the K-values generated by Wilson correlation at conditions of HPRT0 tests with the compositional K-values generated through the suggested methodology in this

study. The results suggest that the K-values generated by Wilson correlation are considerably overestimated. While the inaccuracy of the Wilson correlation at lower temperatures is apparent for lighter fractions of oil, the heavier fractions' Wilson K-values deviate noticeably from the compositional K-values with temperature.

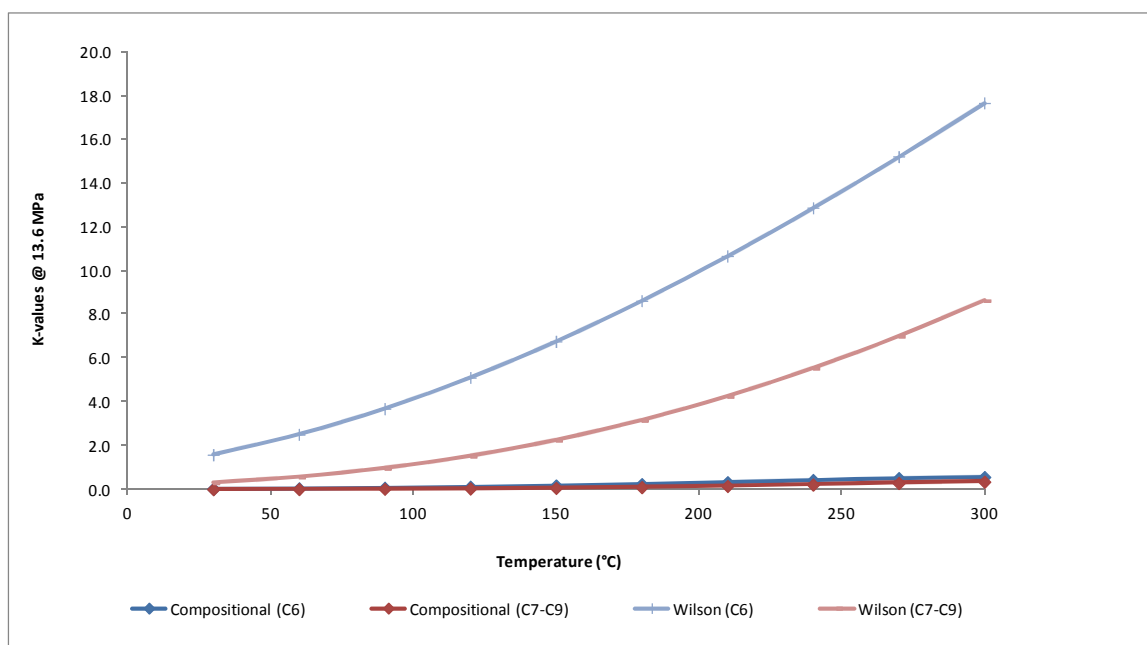


Figure 6-5: Compositional and Wilson K-values for pseudo components C₆ and C₇-C₉

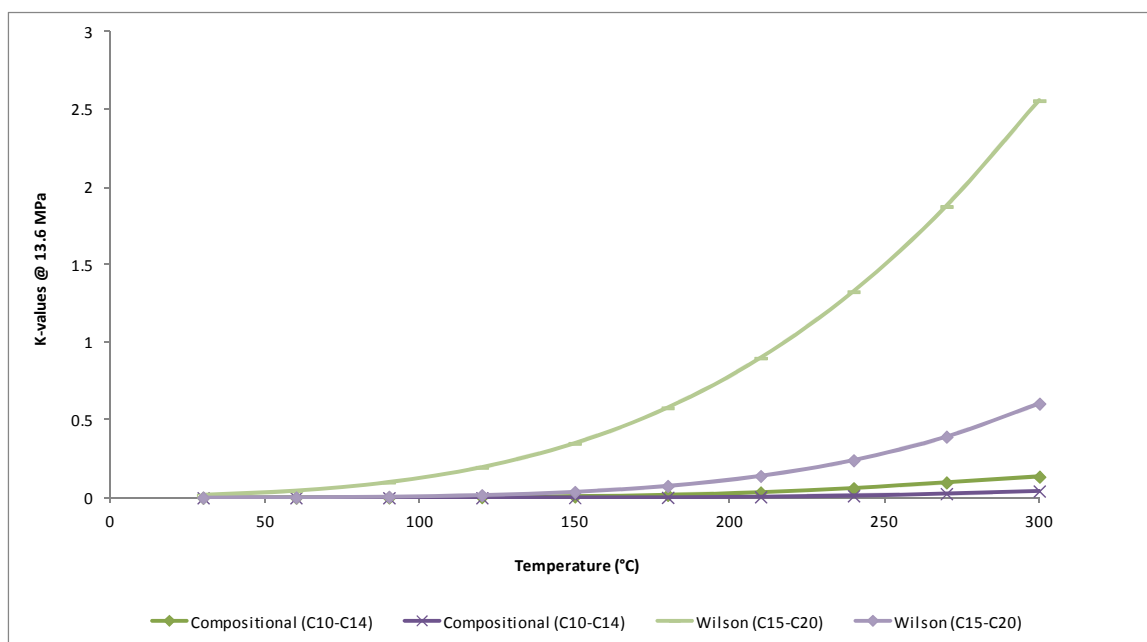


Figure 6-6: Compositional and Wilson K-values for pseudo components C_{10} - C_{14} and C_{15} - C_{20}

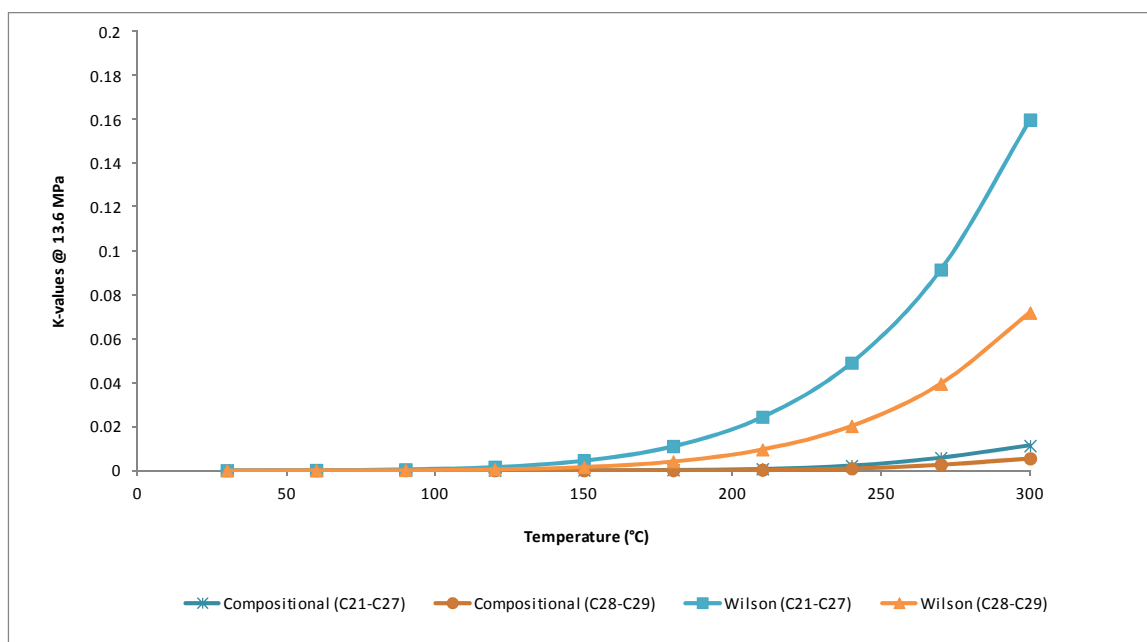


Figure 6-7: Compositional and Wilson K-values for components C_{21} - C_{27} , C_{28} - C_{29} , and C_{30}^+

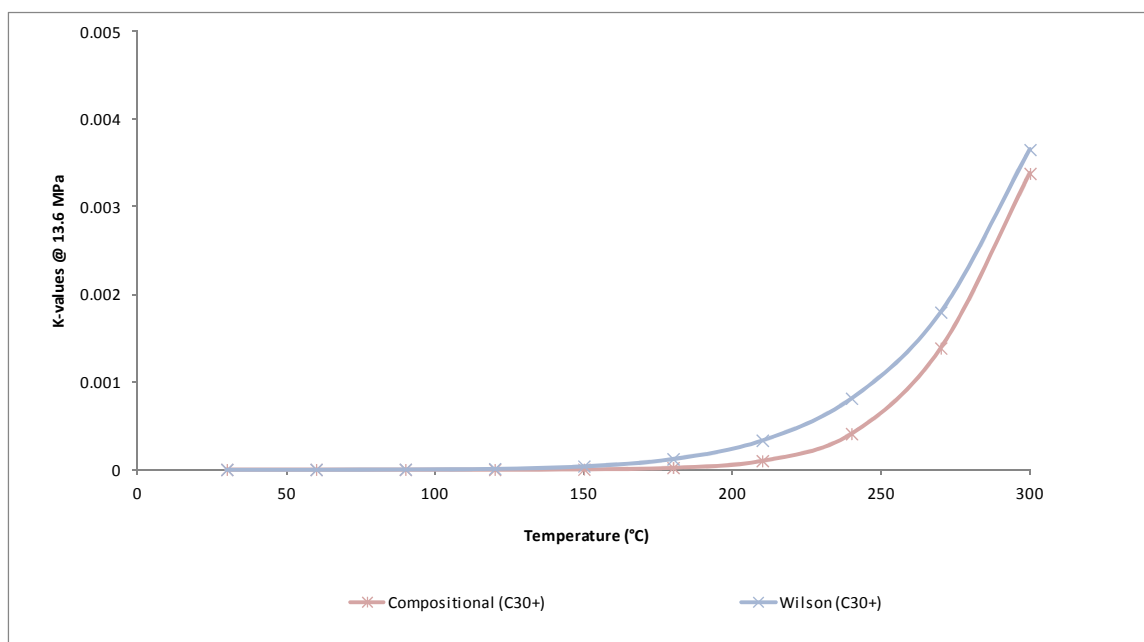


Figure 6-8: Compositional and Wilson K-values for component C_{30}^+

The compositional K-values obtained from the hypothetical flash drums model were employed to get an insight into how the air/fuel ratios inside the reactor change during the air injection tests. Figure 6-9 compares the calculated air/fuel ratios at interval temperatures for Test 2 (Oil A), Test 10 ($n\text{-}C_{15}H_{32}$), and Test 11 ($n\text{-}C_{15}H_{32}$ with no interstitial water). Obviously the calculated air/fuel values are only estimations since the vapor phase fuel composition in the hypothetical model is only given by the K-values and the effect of the reactions are not included. However, during an air injection tests, the oxidation/combustion and cracking reactions impact the amount of fuel in the vapor phase. Nevertheless the estimated air/fuel ratios are useful in terms of signifying the path of the vapor phase kinetics. It can be noted in Figure 6-9 that the air/fuel ratio for both Oil A and $n\text{-}C_{15}H_{32}$ only falls below 20 and into the flammable range at temperatures above 150 °C. Richness of the fuel is apparent above 250 °C. In Chapter

7, the actual air/fuel ratios are reported. These values are calculated based on the predicted compositions by the comprehensive simulation model.

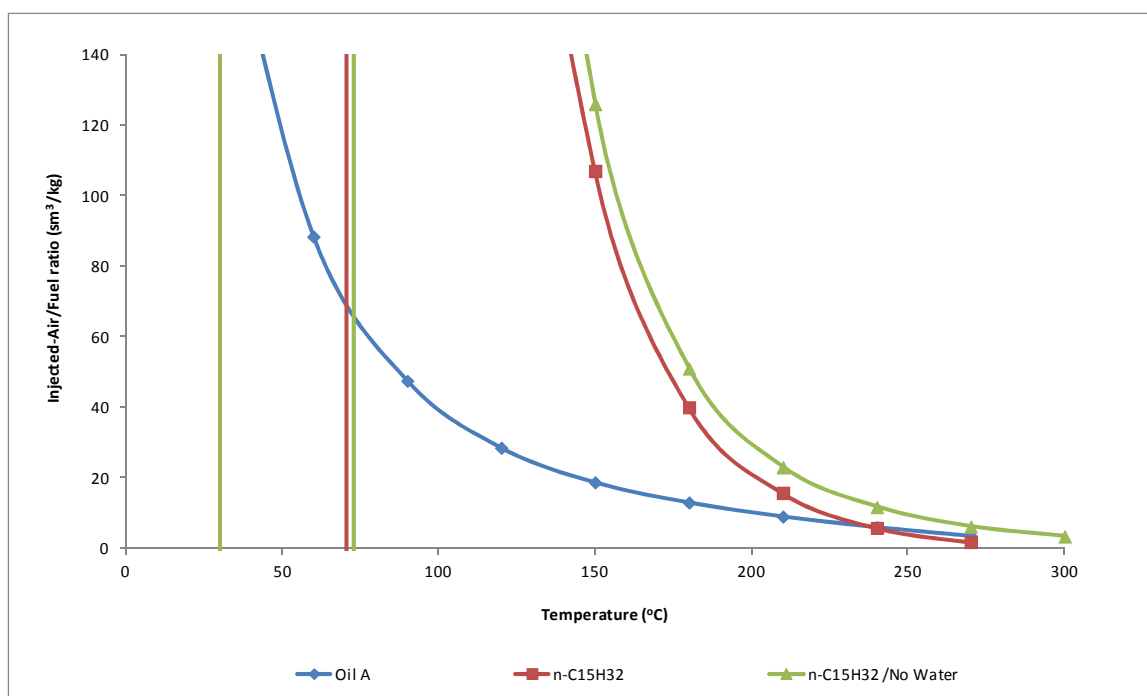


Figure 6-9: Estimated air/fuel ratios using the compositional K-values for the air injection Test 2 (Oil A), Test 10 ($n\text{-C}_{15}\text{H}_{32}$), and Test 11 ($n\text{-C}_{15}\text{H}_{32}$ / no water)

Chapter Seven: Numerical Simulation

In this chapter the numerical simulation models that were built, validated and refined to represent the air injection and nitrogen injection tests performed on the HPRT0 setup are described. Also new findings, mostly concerning the oxidation/combustion reaction kinetics, obtained from the numerical study are discussed. STARS (2009.11), a commercially available advanced thermal simulation package provided by Computer Modeling Group (CMG), was used to simulate the experimental air and nitrogen injection data. The EOS based fluid model obtained from the characterization scheme, reviewed in Chapter 6, was used in the STARS models. It is assumed that thermodynamic equilibrium prevails in the grid blocks. Distribution of the components between the oil and gas phase is defined by the compositional K-values which were obtained through the developed methodology explained in Chapter 6. Given the oxidation/combustion reactions being active, the compositions are also influenced by the defined reaction kinetics. Since the combustion reactions may be active in the vapor phase, if a flammable mixture composition exists within that phase, there is a strong link between the K-values and reaction kinetics or in other words between the evaporation and oxidation/combustion phenomena inside the reactor.

Essentially, the main purpose of this simulation study is to use a numerical model to match the experimental results through an adequate kinetics model. In order to make this possible, all other factors such as relative permeabilities, K-values, thermal properties, and heating values needed to be tuned in the absence of a reaction model. This is why the nitrogen injection tests were performed as the preliminary experimental tests and later were used to tune the simulation parameters exclusive of the ones required by the reaction kinetics. Also results of the nitrogen injection simulations can be

definitive concerning how close the conditions in the system may be to the thermodynamic equilibrium and under what conditions this assumption may be valid.

7.1 General input data

The reactor was modelled with a one-dimensional Cartesian 58 or 56 grid blocks depending on length of the reactor (490 mm for Tests 1-9 and Test15, 460 mm for Tests 10-14). All grid blocks had the same equivalent square cross sectional area normal to direction of the flow. The flow was against the Z direction since the gas flow in the reactor is downwards (Figure 7-1). An absolute porosity of 40% and permeability of 4 Darcy was set equal for all grid blocks. The sand pack was expected to have high porosity and permeability considering the nature of the unconsolidated sand. Initial water and oil saturation were the same for the saturated blocks. For the inlet and outlet blocks, packed with coarse sand, saturations were set to zero.

The number of the grid blocks was arrived at by starting with a primary number of cells based on the proportion of the length and cross sectional area of the reactor. Then the grids were refined in steps to a final level where no further change in model results were observed. While nitrogen injection tests did not show much sensitivity to the grid size when changed by the order of $\frac{1}{2}$ and 2, air injection tests were sensitive to size. The temperature profiles in the air injection tests were more accurate when the numbers of the grids were doubled. However, further refining of the grids was less effective, having considered the increased run time for the simulator. It is worth mentioning that refining of the grids only had a slight quantitative effect on the results of the process; nevertheless, qualitative results remained unchanged. Figure 7-2 shows how the results of the 25 cell and 58 cell models compare in terms of predicting the temperature history of the air injection Test 2. The 25 cell model could not handle

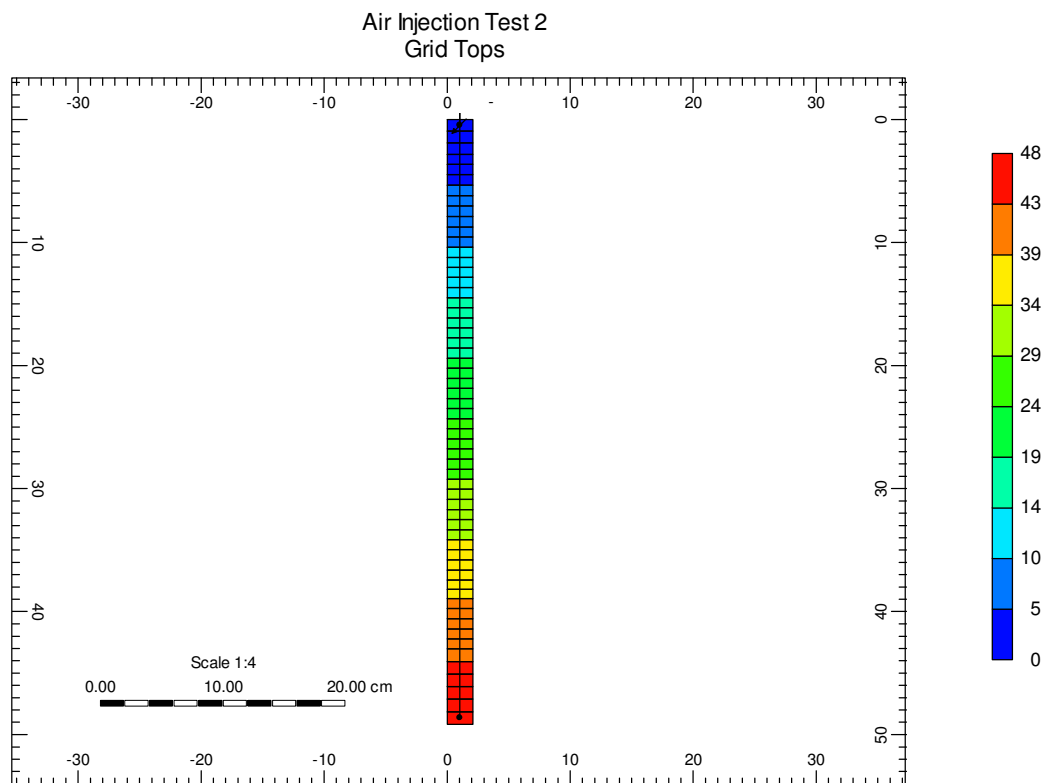


Figure 7-1: Schematic of the simulation grid blocks for Test 2 (58 cells)

heat losses properly. This is indicated by the long period of time needed for each combustion zone to lose its exothermic heat after passage of the combustion front. However the 58 cells model could present an acceptable simulation of the temperature profiles. In order to justify if 58 cells were sufficient enough, a 112 cells model was also examined. Figure 7-3 compares the temperature histories of Test 2 obtained by 58 and 112 cells simulation models. Expectedly further refining of the grid cells, which contributes to a better heat transfer model, led to slightly better predictions of the temperature. This can be observed at higher temperatures where effect of heat loss becomes more significant. Generally, the temperature in a combustion zone is the most sensitive parameter to the size of the grid cells, due to a rapid temperature rise in a small combustion zone. Since the 58 cells and 112 cells models could generate

temperature results that were acceptably close to the experimental data of Test 2, the 58 cells model was preferred for the rest of the simulation study, considering the trade off between computing time and accuracy.

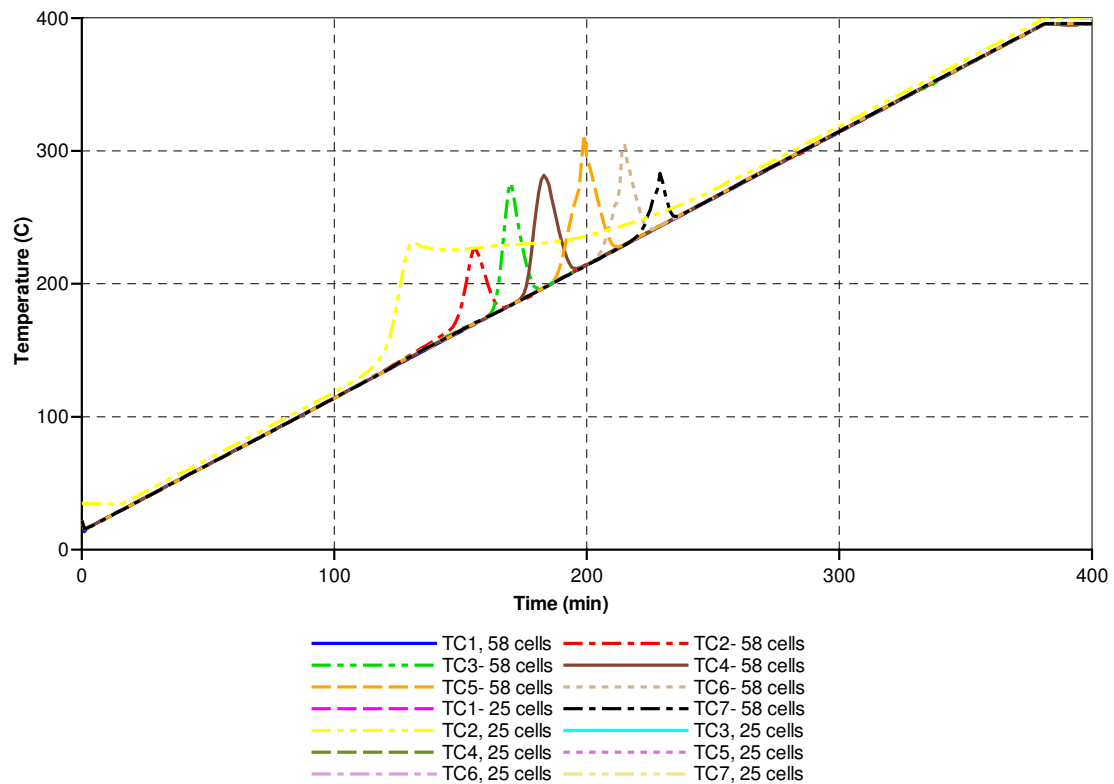


Figure 7-2: Comparison of the temperature histories of Test 2 predicted by the 58 cell and the 25 cell simulation models

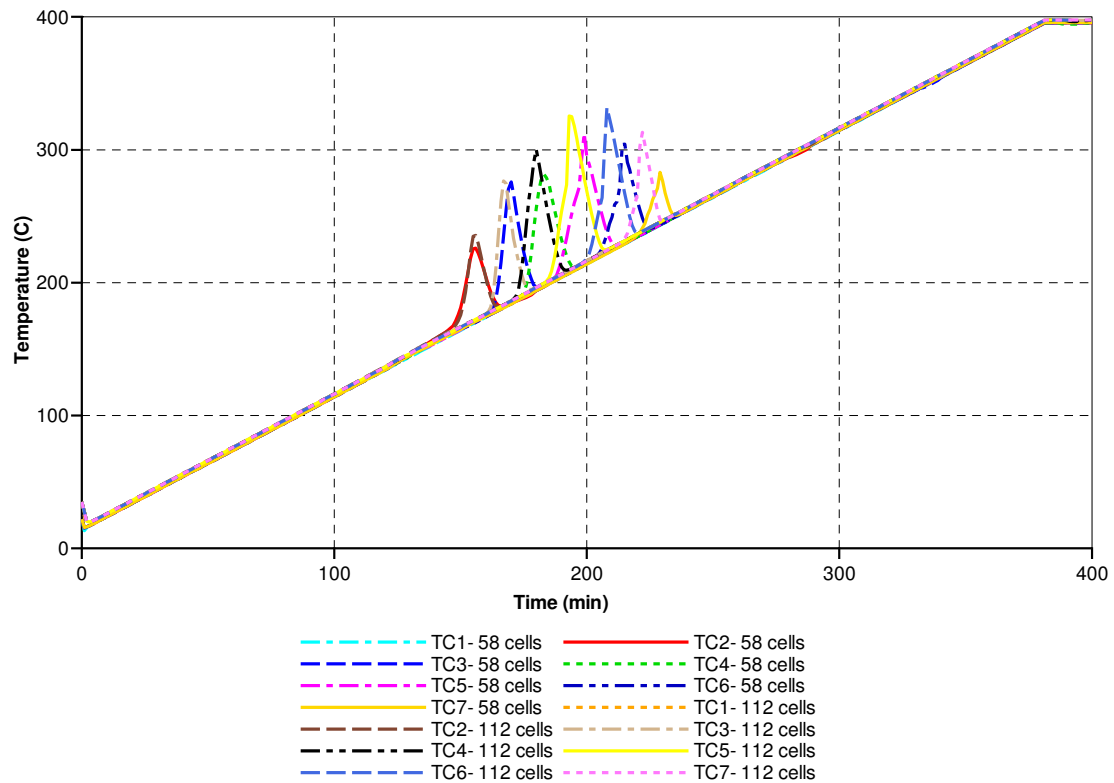


Figure 7-3: Comparison of the temperature histories of Test 2 predicted by the 58 cell and the 112 cell simulation models

Cumulative oil productions predicted by the 25, 58, and 112 cells models were also compared in one plot (Figure 7-4) with respect to the temperature history of Test 2 obtained through the 58 cells model. While the 25 cells model presented a poor prediction of the oil production, the 58 and 112 cells models showed very close cumulative oil values as 9.6 g and 8.9 g respectively. It was reviewed in Chapter 4 that the experimental oil production of Test 2, although being measured as 8.6 g, was not accurate and some of the produced oil (up to 1.9 g based on material balance) was lost. So, the 58 cells model was selected for the simulation study.

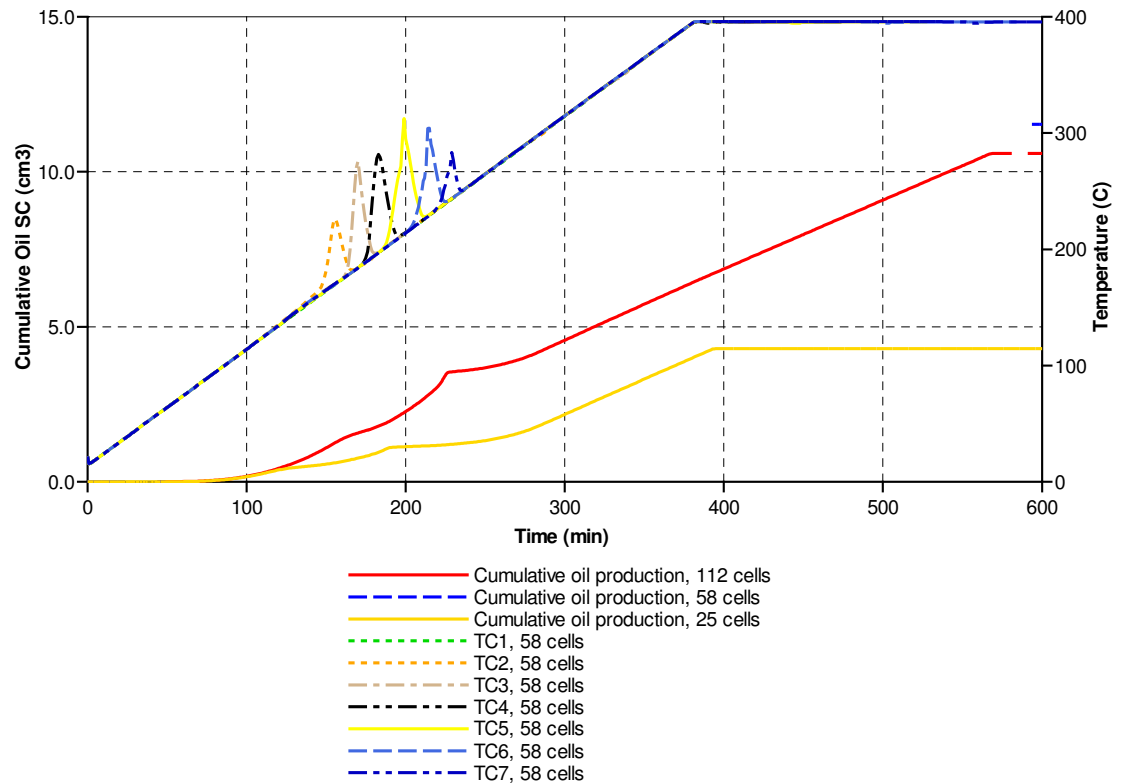


Figure 7-4: Cumulative oil production of Test 2 predicted by 25, 58, and 112 cells models with respect to the temperature history

7.1.1 Rock-fluid data

Figure 7-5 and Figure 7-6 show the relative permeabilities for the water/oil and liquid/gas systems. The three phase relative permeabilities were set to be calculated using Stone-II model in STARS. The original relative permeability curves were obtained from a study conducted by Niz-Velasquez (2009) for the purpose of which a specialized core flood set up was used to perform sequential injection of oil (Oil A), gas and water at reservoir pressure. Pressure drop across the core and fluid volumes at room condition were recorded. Then, JBN (Johnson, Bosler, and Naumann; 1959) technique was applied to the processed data to determine the relative permeabilities. Next a compositional simulator (GEM) was employed to simulate the displacements and relative

permeabilities were adjusted to reproduce the pressure drop and cumulative volume data. Although these sets of relative permeabilities were obtained using Oil A, a water-wet sandstone core was used. On the other hand, the HPRT0 tests performed for the purpose of this study utilized original carbonate core from the reservoir of Oil A. It is noted that the rock properties are very important in measuring of the relative permeabilities. So, the relative permeabilities from the previous study were adjusted to match the production and temperature data of the nitrogen injection tests. Basically the curvature and endpoints were enhanced to meet the requirements of the unconsolidated mixed-wet core of this current study.

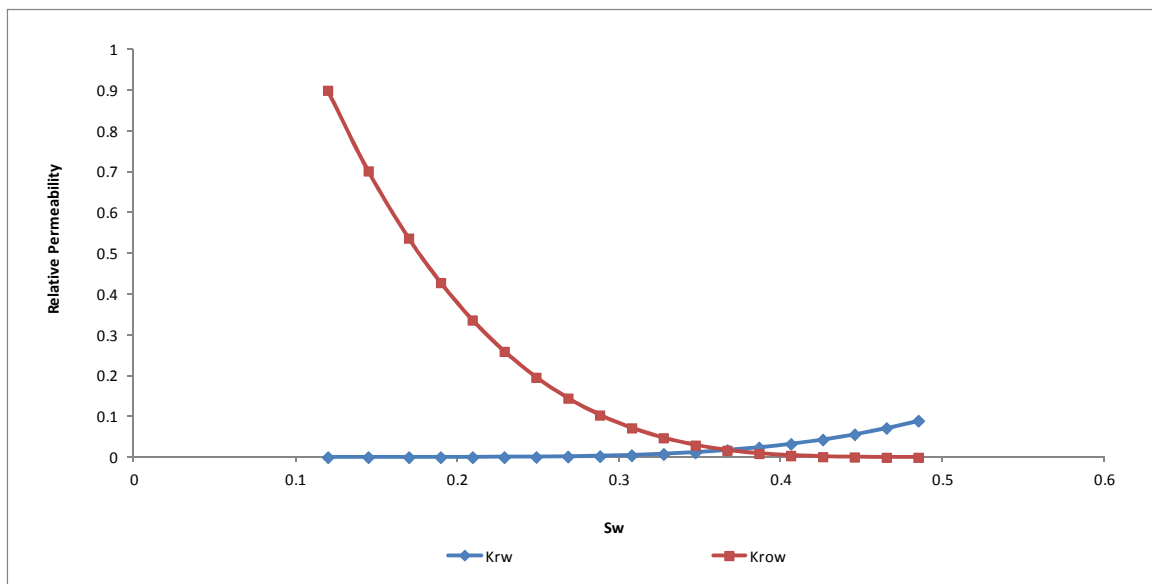


Figure 7-5: Relative permeabilities to water and oil with respect to water saturation

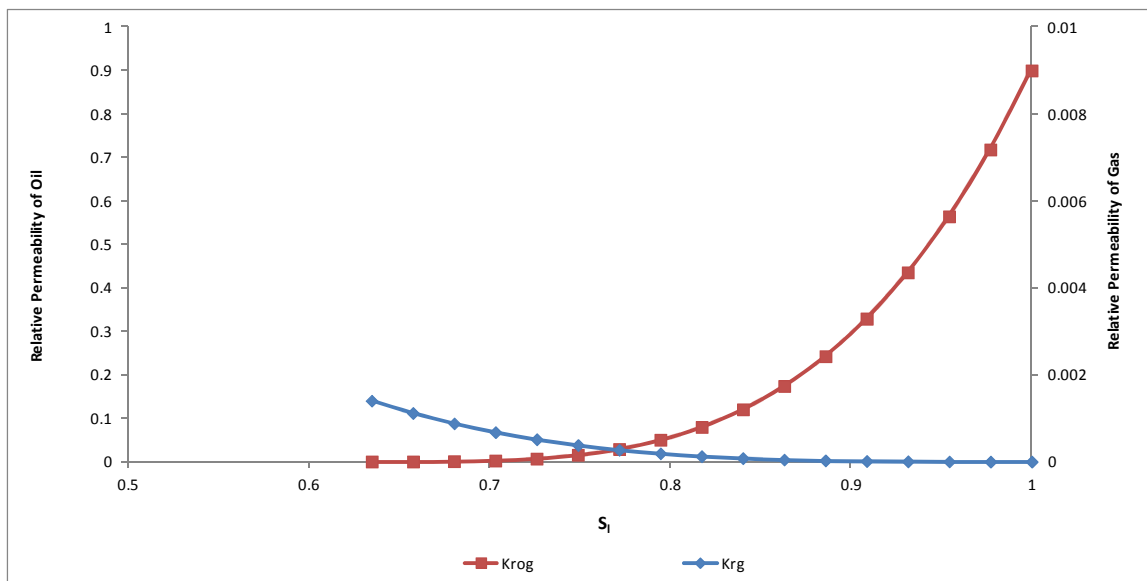


Figure 7-6: Relative permeabilities to oil and gas with respect to liquid saturation

The option of temperature dependant relative permeabilities in STARS was considered for this model. However, since the Oil A rock is mixed-wet to water-wet this option did not affect the results of simulations performed on the system of Oil A, Brine, and Oil A rock.

7.1.2 Fluid model

The fluid model described in Chapter 6 was generated with Winprop. The liquid model consisted of nine pseudo components for the purpose of the preliminary phase behavior study. However, definition of nine liquid pseudo components alongside the three gas phase components (O_2 , N_2 , and CO_x) is not efficient in terms of processing time. Although run time is not an issue when simulating the HPRTO tests, application of the kinetics model to a field scale simulation will not be feasible if the number of pseudo components is not reduced to a more practical value. Commonly in the *in situ* combustion modelling, liquid oil is lumped into 2 pseudo components of “heavy oil” and “light oil” consisting of the heavier and lighter fractions of oil respectively. The defining

limit between these two components normally depends on type of the oil and C_7^+ is normally grouped as one “heavy oil” component in lower gravity oils. On the other hand high gravity oils, which are candidates of HPAI, consist of higher quantities of light oil fractions and thus need more precise component characterizations due to component-dependency of evaporation (K-value) and reaction kinetics (vapor phase reactions).

For the purpose of the simulation of the high pressure ramped temperature air injection and nitrogen injection tests undertaken in this study, the 7 liquid oil pseudo components of the phase behavior model were further lumped into three pseudo components. The suggested lumping scheme was based on Oil A’s carbon number distribution (Figure 3-5) as well as simulated distillation results of the produced oil from nitrogen injection Test 13 on Oil A where no connate water was initially present (Figure 5-24). Table 7-1 presents the suggested lumping scheme, showing how the 7 pseudo components (C_6 , C_7 - C_9 , C_{10} - C_{14} , C_{15} - C_{20} , C_{21} - C_{27} , C_{28} - C_{29} , and C_{30}^+) were lumped into 3 pseudo components, namely LO, MO, and HO.

Table 7-1: Lumping scheme for nitrogen and air injection simulation models

7 Pseudo-components Winprop Phase behavior model	3 Pseudo-components STARS air and N2 injection models	Molecular Weight (g/gmol)	Mole Fraction
C_6	LO (Light Oil)	105	0.28
C_7 - C_9			
C_{10} - C_{14}	MO (Medium Oil)	189	0.51
C_{15} - C_{20}			
C_{21} - C_{27}	HO (Heavy Oil)	418	0.21
C_{28} - C_{29}			
C_{30}^+			

As a sensitivity evaluation, nitrogen injection Test 1 was modelled with both the 3 and 7 pseudo component liquid models. Figure 7-7 compares the outcomes of the two simulation models in terms of temperature history, cumulative oil production and cumulative water production. Prediction of the temperatures and water production by both models were identical; however the oil production profiles showed a slight acceptable difference. The cumulative produced oil for the 7-component model was 14.2 cm³ and for the 3-component model was 12.4 cm³ by the end of runtime of 350 minutes. The volume of collected oil in Test 1 was 12.2 cm³ as reported in Table 4-1. According to the experimental error in liquid collection system, it was discussed in Chapter 3 that the amount of collected liquid was undermeasured in Test 1. Both of the 3-component and 7-component models predict the oil production within the error range of the system, and thus verify the 3-component liquid oil model for incorporation into the STARS simulation models of air and nitrogen injection tests.

7.1.3 Heating process

Heating of the reactor for simulation of the ramped temperature tests was modeled through a proportional heat transfer coefficient and a temperature set point for each time step. The temperature set points were defined according to the experimental heating rate and the temperature of the reference thermocouple (TC1). A proportional heat transfer coefficient (J/min °C) was assigned to the “UHTR” keyword in STARS and temperature set points were given to “TMPSET”. The rate of heat gain was calculated as the product of UHTR and (TMPSET-T) when TMPSET was bigger than T (instant temperature of the cell). However upon arrival of the oxidation/combustion front at a zone, T exceeded TMPSET and heat gain was automatically set to zero. The conductive heat loss to the metal jacket enclosing the reactor was estimated by using “HEATR”. HEATR (J/min) is a constant heat transfer rate that is designed to be used in conjunction

with “UHTR” and “TMPSET” in STARS. However, HEATR can offer a constant rate of heat loss where the actual rate of heat loss depends on the temperature. Basically, more heat loss is expected from the combustion zones at higher temperatures which is not quite satisfied with a constant heat loss model. But, the predicted temperatures, as will be reviewed, although not 100% accurate in peak values still mimicked the overall behavior of the oxidation/combustion reactions during the test. It is worth mentioning that the thermal conductivity of rock, water, oil, and gas were set to 0.8, 0.37, 0.8, and 0.08 J/min-cm-°C respectively.

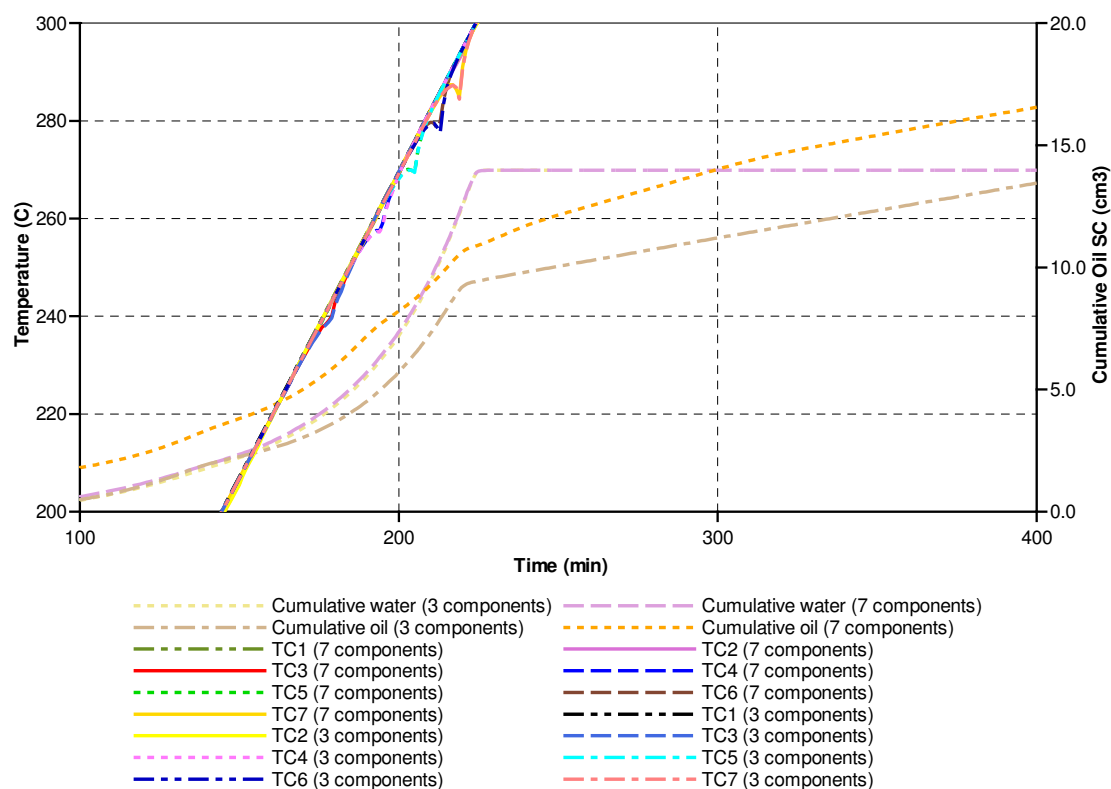


Figure 7-7: Comparison of temperature histories and cumulative oil and water productions in the two simulation models consisting of 3 and 7 liquid oil components

7.2 Simulation of the nitrogen injection tests

This section includes results of the simulation runs performed to model Test 1, Test 5, Test 7, and Test 12. These tests are, respectively, high flux nitrogen injection on Oil A, isothermal nitrogen injection on Oil A, low flux nitrogen injection on Oil A, and high flux nitrogen injection on $n\text{-C}_{15}\text{H}_{32}$ experimental runs. Simulation of the nitrogen injection tests not only allows to study the evaporation and viscous drives in an HPAI process, but also functions like a tuning procedure to the air injection models before the reaction kinetics are added.

Although it was planned to use the same physical reactor for all the tests and also set and maintain the same fixed value of gas injection flux for all high flux and also low flux tests, unfortunately it was not possible to obtain this desirable condition during the course of the experiments. The reactor had to be rebuilt for Test 10 and its length was reduced from 49 cm to 45.6 cm. Therefore the number of grid cells and their average height had to change for Tests 10, 11, 12, 13, 14, and 15. However, this was a minor overall change as the number of grid blocks were reduced from 58 to 56 and their height were slightly reduced to compensate for the reactor length change accordingly. Maintaining an exact value for the injection flux was also not successfully functioned by the mass flow meter (although calibrated) and the actual injection rate measured by the wet test meter was used for simulation of every test.

7.2.1 Nitrogen injection Test 1

Nitrogen injection Test 1 which was performed on Oil A was the first experimental run to model. After history matching of the results of this model against the experimental data and achieving the final satisfactory results, this model was used as a base model for simulating the other tests.

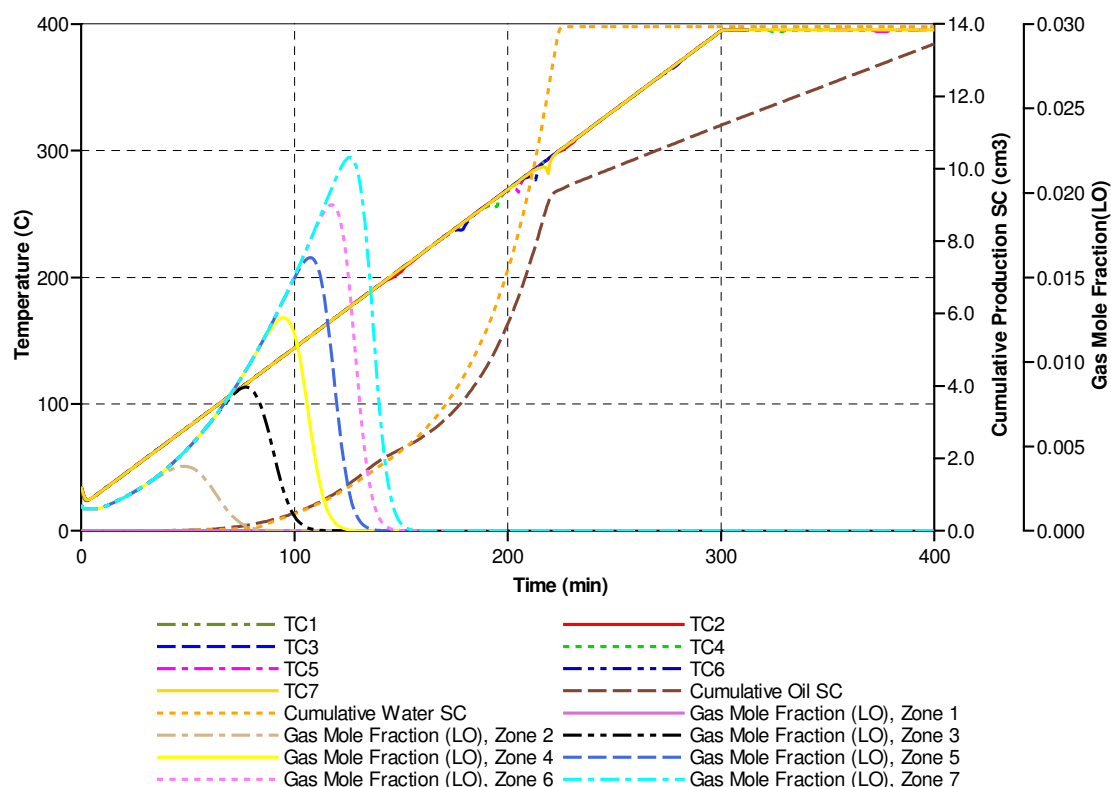


Figure 7-8: Temperature history, cumulative oil and water production history, and gas mole fraction of LO component at individual thermocouple zones, as modeled for nitrogen injection Test 1 (Oil A, $38.2 \text{ sm}^3/\text{m}^2\text{h}$).

Test 1 simulation model consisted of 5 components: N_2 , H_2O , LO, MO, and HO. Figure 7-8 presents the simulation results history of Test 1 in terms of temperature and gas mole fraction of the light oil component (LO) at individual thermocouple zones together with the cumulative volume of the produced liquid for this test. It must be noted that STARS automatically considers every vapor component as a “gas” component. A distinct evaporation front can be observed in Figure 7-8. The period of time (90 minutes) over which the evaporation front formed and developed was exactly the same as observed in the experimental results. However, the onset of formation was delayed by 10°C (8 minutes on a ramp of $^\circ\text{C } 75/\text{h}$) in the simulation run. Velocity of the evaporation

front for the last three dips calculated as 0.34 m/h which is very close to the experimental velocity of 0.32 m/h which was shown in Figure 5-1. The average temperature drop in all zones was predicted as 7 °C which was identical to the experimental value. Yet, the 10 °C shift for the onset of the evaporation indicated that the generated K-values by the phase behavior model were not perfect. A precise set of K-values could be obtained only with minimum lumping of the oil components, where the critical properties of the pseudo components were least deviated from the actual value through the lumping and combining process.

Figure 7-8 also includes the histories of LO gas mole fraction at individual zones. It can be noticed that the light fraction of Oil A labelled as LO (up to C₁₀) traveled through the reactor and was produced before the formation of the distinct evaporation front. Obviously, the amount of LO and its low latent heat value had not been sufficient to cause a visible temperature drop within the heating process and thermal properties of the reactor system.

Since formation of the exothermic oxidation/combustion front was observed in Chapter 5 to coincide with the formation of the evaporation front, it had to be considered in reaction kinetics development stage that the LO portion of Oil A was not available for participation in the vapor phase reactions, unless it later was produced through cracking reactions. Figure 7-9, Figure 7-10, and Figure 7-11 show that the visible evaporation front was mainly formed by MO and water. It can be observed in Figure 7-9 that mole fraction of water increased in a particular zone with temperature (through evaporation) until the arrival of the evaporation front at that zone. At this temperature all of the water molecules transferred from the liquid phase to the vapor phase, leaving the saturation of water in that zone as zero. The sharp drop at the leading edge of the gas water saturation curves indicated that the gas phase could allocate sufficient saturation to

water so that it could contain and carry all the water vapor molecules. In other words the flux of gas injection was high enough to enable this to happen.

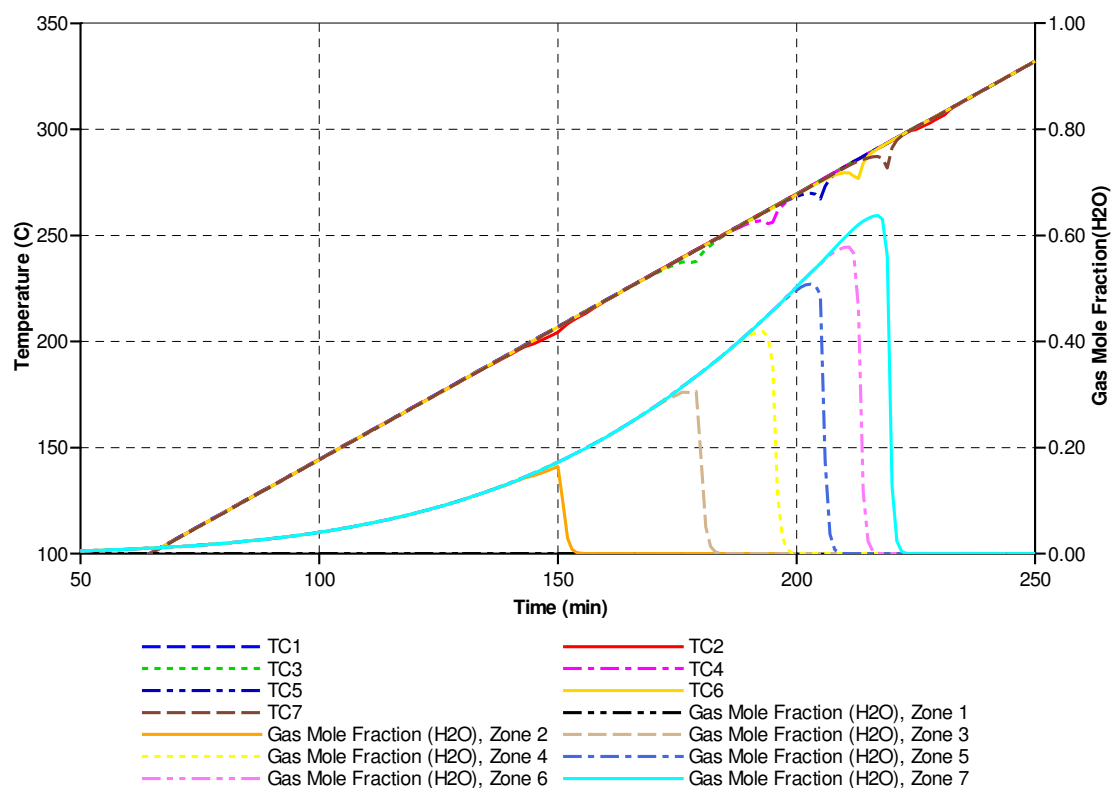


Figure 7-9: Gas mole fraction of water component at individual thermocouple zones with respect to the temperature history, as modeled for nitrogen injection Test 1 (Oil A, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

Figure 7-10 presents the histories of the MO gas phase mole fraction at individual zones. It is noted in this plot that all the initial MO fraction of Oil A evaporates during the passage of the evaporation front through the reactor. Now, what remains in the liquid phase after the evaporation front has swept the entire reactor is the heavy portion of the oil or HO. This can be observed in Figure 7-11 and Figure 7-12. Being dictated by the K-

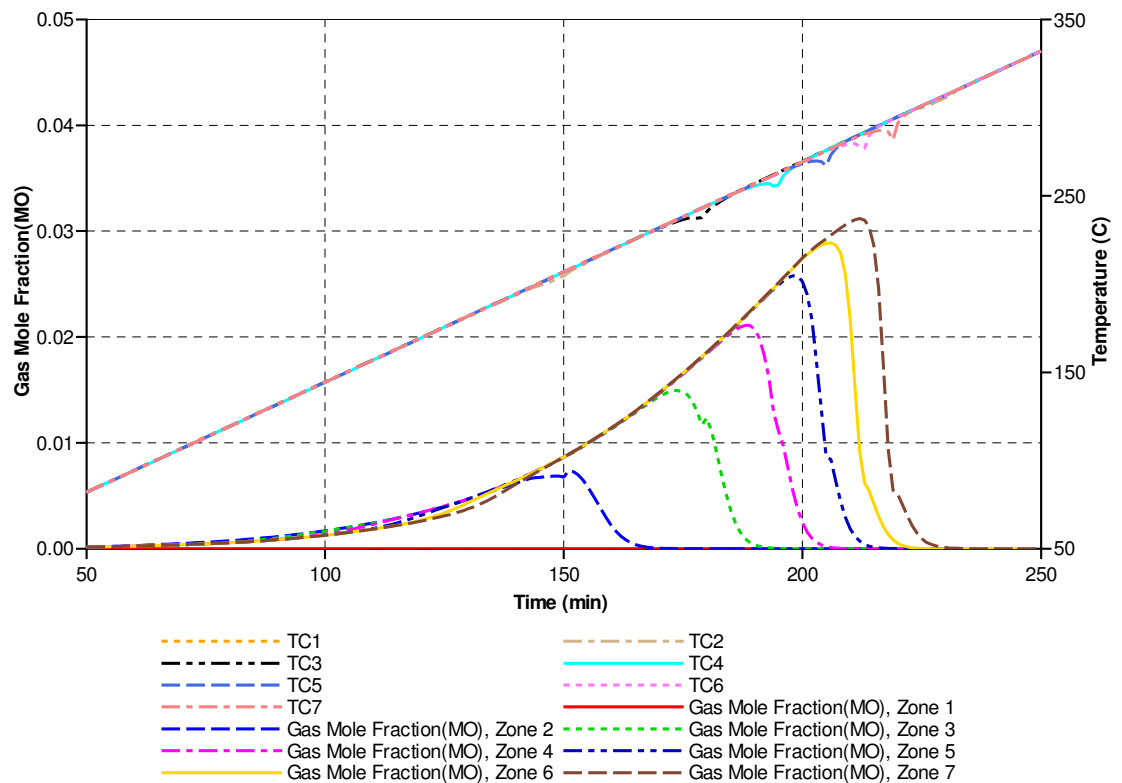


Figure 7-10: Gas mole fraction of MO component at individual thermocouple zones with respect to the temperature history, as modeled for nitrogen injection Test 1 (Oil A, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

values, heavier fractions of oil evaporate at higher temperatures. Although Figure 7-11 shows that there's an increase in the HO gas mole fraction during the advancement of the evaporation front, this is a consequence of the decline in the MO gas mole fraction and not necessarily more evaporation of the HO. As long as HO molecules exist in the liquid phase in a zone, a portion of them evaporate on a constant rate according to the injection flux. The constant rate is implied by the rectangular shape of the gas and liquid HO mole fractions in Figure 7-11 and caused by constant nitrogen flux, constant temperature (at this point of the test) and single HO oil component in the liquid and gas phases.

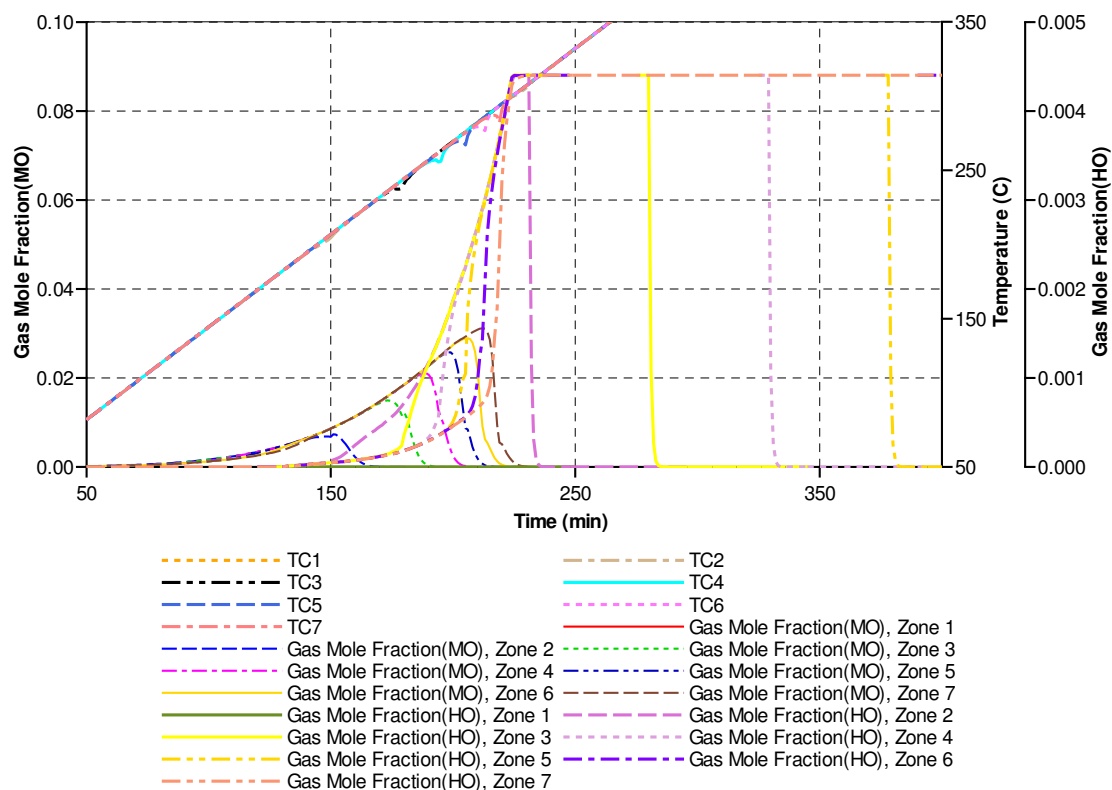


Figure 7-11: Gas mole fraction of MO and HO component at individual thermocouple zones with respect to the temperature history, as modeled for nitrogen injection Test 1 (Oil A, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

Total liquid production for Test 1 was predicted as 11.37g (13.38 cm^3) for oil and 13.92 g (13.92 cm^3) for water respectively. The total experimentally collected oil from Test 1 was 10.24 g; however, material balance for Test 1 indicated a 16% oil loss which together with 10.24 g of collected oil would sum up to 12.54 g of total expected oil production.

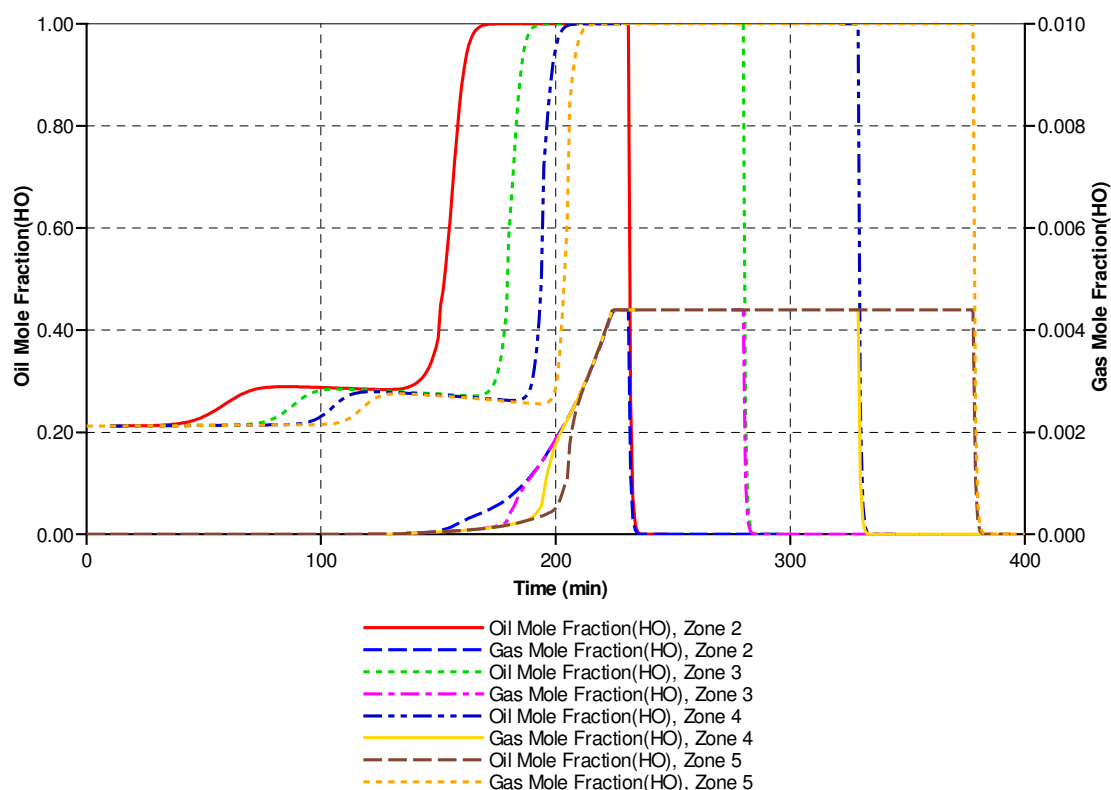


Figure 7-12: Gas and oil mole fractions of HO component at individual thermocouple zones with respect to the temperature history, as modeled for nitrogen injection Test 1 (Oil A, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

The 11.37 g of oil predicted by the simulation model, therefore, falls in the acceptable range of the experimental data. The same story goes with the water production which had a 23.5% experimental material balance error. Thus, the overall performance of the high flux nitrogen injection simulation model showed to be reasonable and results were considered as satisfactory.

7.2.2 Nitrogen injection Test 5

In order to exclude the evaporation drive mechanism and effect of K-values (and temperature) and evaluate the sole effect of viscous drive through relative permeabilities, isothermal nitrogen injection Test 5 was simulated. Figure 7-13 depicts the temperature history and cumulative production history of Test 5 in the same plot. 3.2 grams (3.8 cm^3) of total oil production was predicted by the model and the experimental value was 2.9 g for Test 5. Also the model predicts 7 g (7 cm^3) of water production for this Test while the experimentally collected water was only 2.3 g. Considering the notable experimental material balance error for Test 5, the overall performance of the relative permeabilities was reasonable.

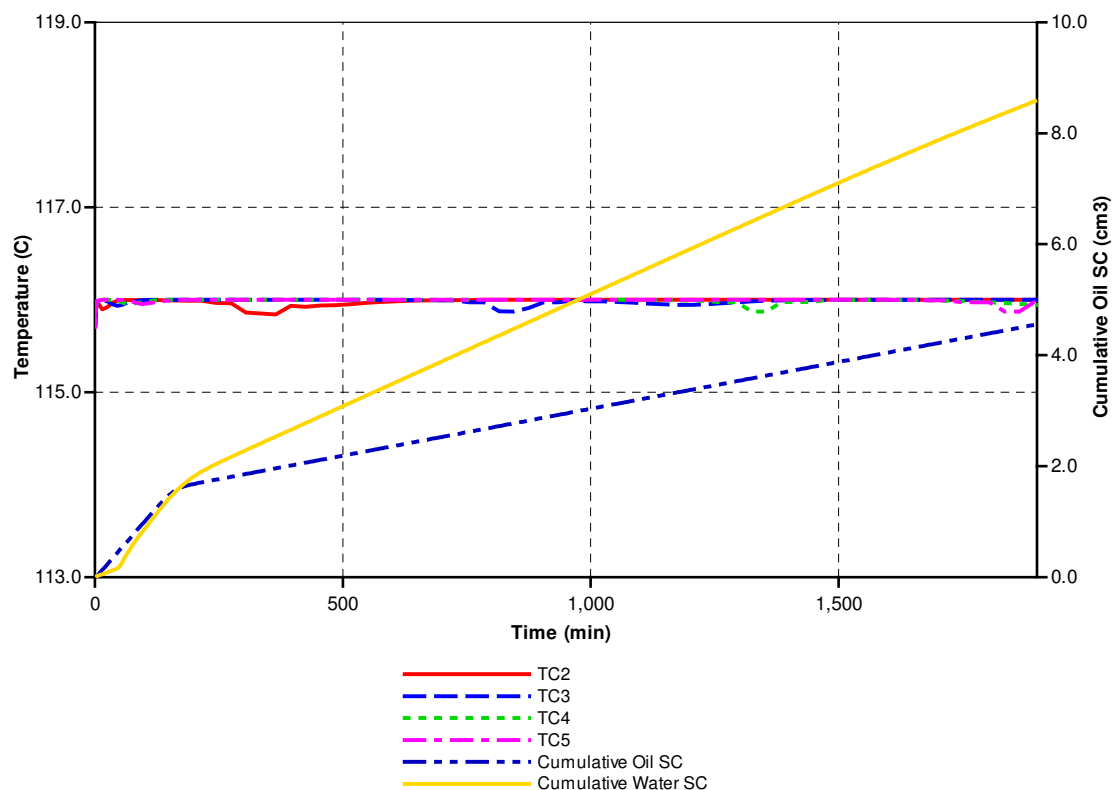


Figure 7-13 Temperature history and cumulative oil and water production history as modeled for isothermal nitrogen injection Test 5 (Oil A, 38.2 sm³/m²h)

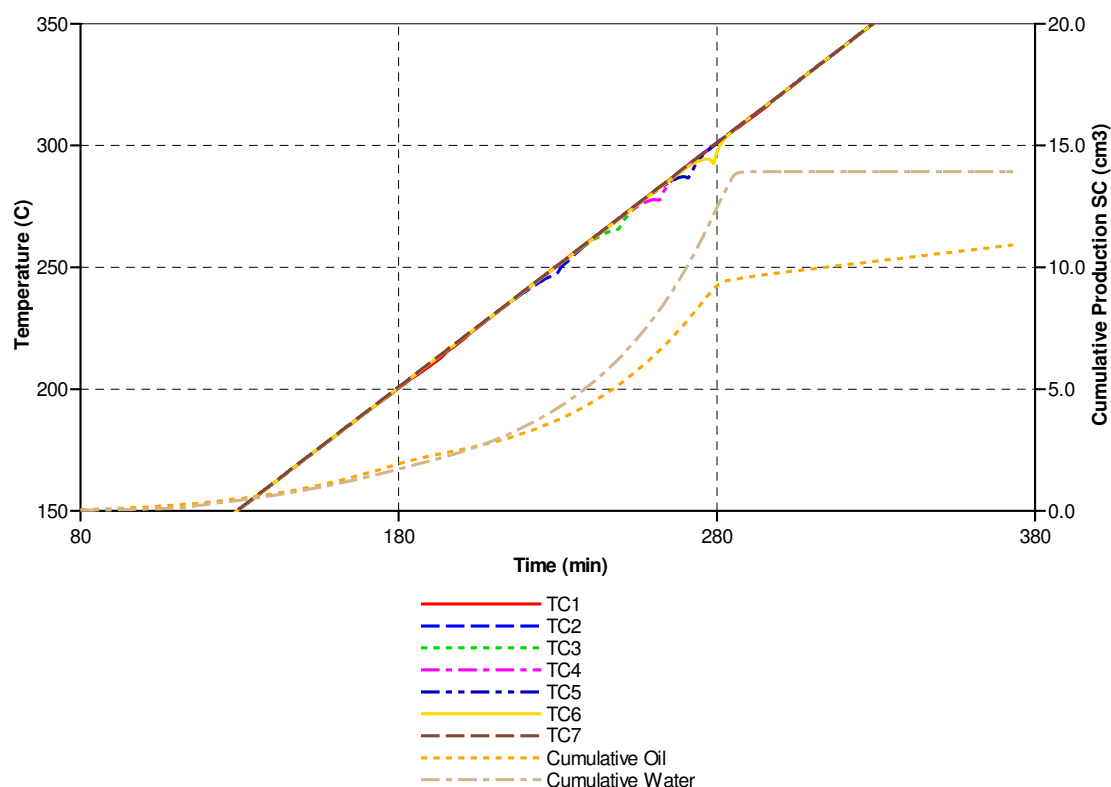


Figure 7-14: Temperature history and cumulative oil and water production history as modeled for low flux nitrogen injection Test 7 (Oil A, $12.7 \text{ sm}^3/\text{m}^2\text{h}$)

7.2.3 Nitrogen injection Test 7

Low flux Test 7 was intended to be run under a gas injection flux of $12.7 \text{ sm}^3/\text{m}^2\text{h}$ which is one third of the base case high injection flux of $38.2 \text{ sm}^3/\text{m}^2\text{h}$. However the performance of the mass flow meter was not reliable and the wet test meter measurements of the produced gases indicated a flux of $25.4 \text{ sm}^3/\text{m}^2\text{h}$ which is two third of the base case flux. Therefore, for the simulation model of Test 7 the flux based on the wet test meter was used as input data. Temperature history in Figure 7-14 shows a very similar trend to that observed for simulation results of high flux Test 1. Although the average temperature drop at the individual zones and also the duration over which the advance of the visible evaporation front was completed in the reactor were very close to

the experimental data, onset of formation of the visible front was predicted at a 13 °C lower temperature. Precise production data were achieved by the simulation model. It was mentioned in Chapter 4 that the liquid collection system was improved for Test 7 and the material balance error was reduced significantly with the new system. So, the experimental production data became much more reliable for Test 7 and the rest of Tests 8 to 15. A total of 8.92 g of oil (10.88 cm³) was predicted by the simulation model while the experimental oil production was 8.85 g. Also the predicted water production and experimental water production were very close, being 13.92 g and 13.72 g respectively. Velocity of the evaporation front while traveling through the last three zones was calculated as 0.34 m/h which is identical to the velocity calculated from the experimental data.

Two hypothetical nitrogen injection simulation models were run to study the sensitivity of the evaporation front velocity to the injection flux and heating rate. Since experimental data on a nitrogen injection test at one third of the base case flux were not available, a simulation model was run under the same conditions of Test 7 but a 12.7 sm³/m²h of injection flux. Simulation results showed that although the onset of the formation of the evaporation front is delayed and temperature drops are smaller when lowering the nitrogen injection flux from two third to one third of the base case flux, the velocity of the front for the last three zones remains almost unchanged. This is in line with observations from lowering the flux from the base case to a two third of base case flux value.

During the experimental study of this thesis it was noticed that the heating ramp rate plays an important role on the results of the tests. This was examined through another hypothetical model which was run under a low (2/3) nitrogen flux but the heating rate was set to 75 °C/h (same as high flux nitrogen Test 1) instead of the base case 60 °C/h of low flux Test 7. A higher heating ramp causes the evaporation front to form earlier and

advance at a faster velocity. Figure 7-15 compares the velocities of the evaporation fronts (through the last three zones) for high flux Test 1, low (2/3) flux Test 7, the hypothetical low (1/3) flux test, and the hypothetical low (2/3) flux high ramp (75 °C/h) test. In the previous chapters when comparing the velocity of different fronts on one plot, time zero was attributed to the onset of the individual fronts. But, in Figure 7-15, time at the first data point is indicating the exact time when the front enters the 4th thermocouple zone. Plotting this way highlights how onset of formation of the fronts happens later (and thus at a higher temperature) as the injection flux is lowered. Also, a higher velocity at a higher heating ramp implies that (as discussed in Chapter 5) velocity of the evaporation is more sensitive to the temperature than the injection flux.

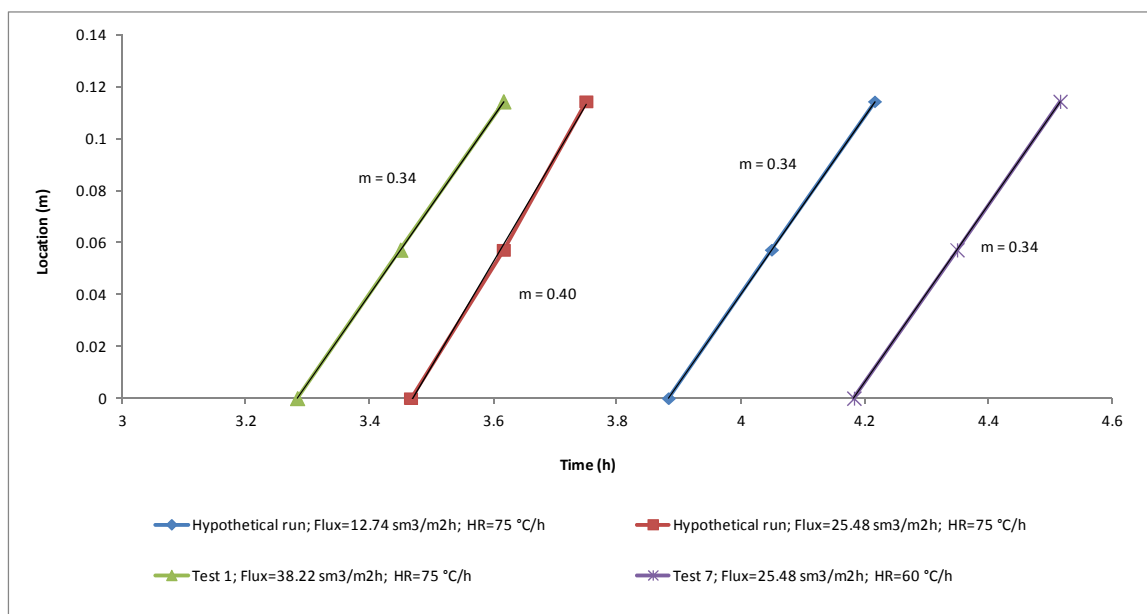


Figure 7-15: Sensitivity of the evaporation fronts' velocities to injection flux (3/3, 2/3, and 1/3 of the base flux) and heating ramp (60 °C/h vs. 75 °C/h)

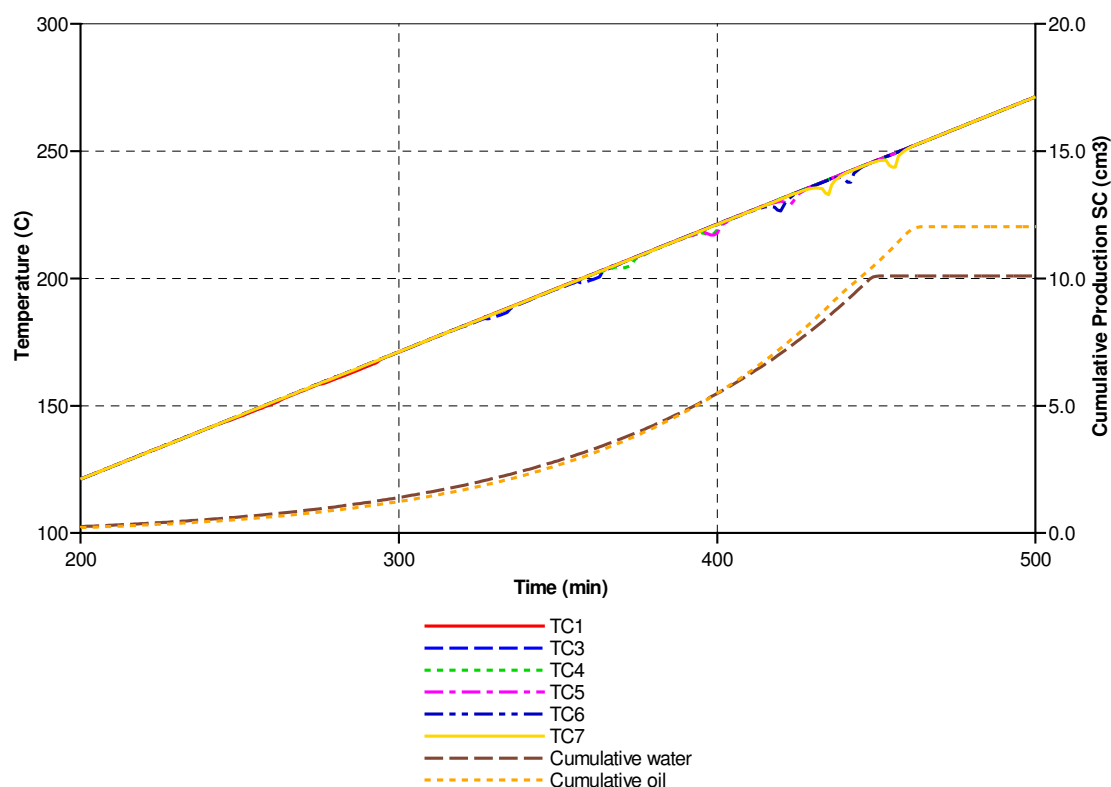


Figure 7-16: Temperature history and cumulative oil and water production history as modeled for high flux nitrogen injection Test 12 ($n\text{-C}_{15}\text{H}_{32}$, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

7.2.4 Nitrogen injection Test 12

Figure 7-16 presents the modeling results of the nitrogen injection Test 12 performed on $n\text{-C}_{15}\text{H}_{32}$. There are two interesting features in this plot. First is the existence of a second evaporation front which starts to form before the first front has passed through the core and continues to advance after the first front has traversed the whole reactor. This was also noted in the experimental data of Test 15. It was shown before that in the Oil A nitrogen injection test what remains in the core after passage of the evaporation front is the heavy fraction of the oil which is mostly not volatile below the 400°C set point temperature of these tests. However this is not the case for Test 12 where all the oil

consists of $n\text{-C}_{15}\text{H}_{32}$. Figure 7-17 clearly shows how the first temperature drop at each zone is caused by evaporation of water and the second dip portrays the evaporation of $n\text{-C}_{15}\text{H}_{32}$.

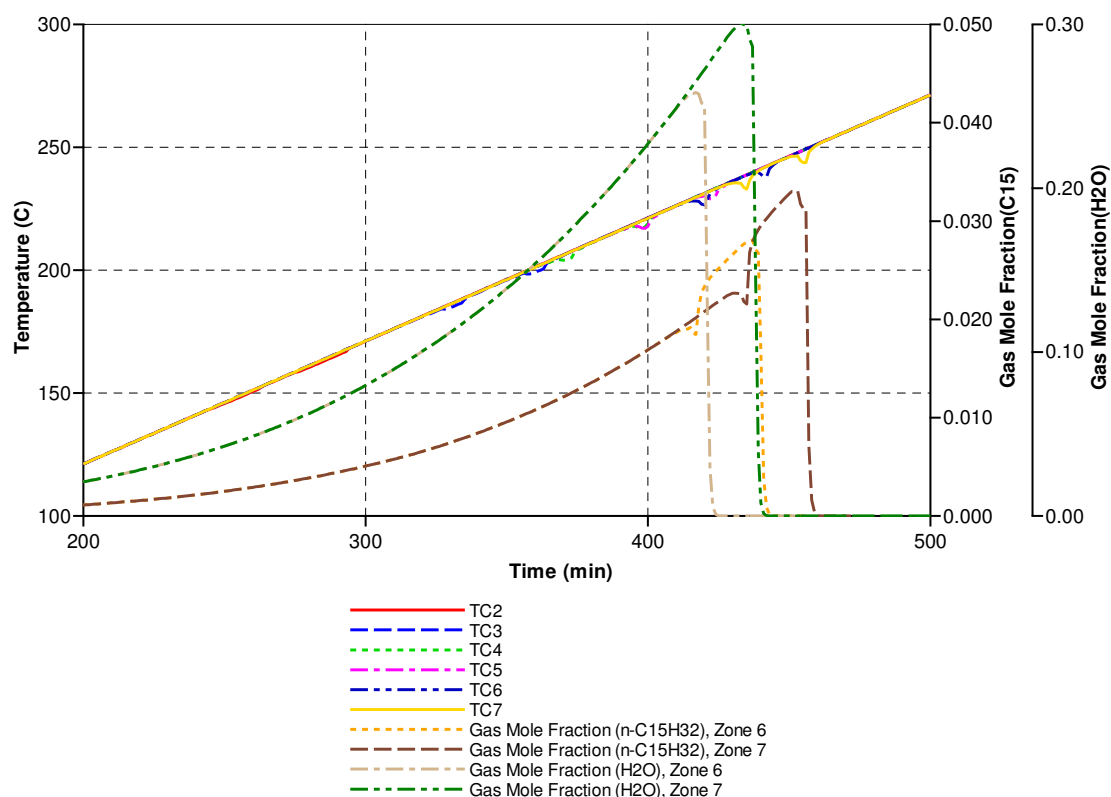


Figure 7-17: Gas mole fractions of $n\text{-C}_{15}\text{H}_{32}$ and water components at the last two thermocouple zones with respect to the temperature history, as modeled for nitrogen injection Test 12 ($n\text{-C}_{15}\text{H}_{32}$, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

For simplicity and readability of the plot, gas mole fraction curves have been only shown for the last two zones in Figure 7-17. As water vaporizes in a particular zone, e.g. Zone 6, most of the vapor phase gets saturated with water molecules due to their lightness in comparison with $n\text{-C}_{15}\text{H}_{32}$. Only a small amount of $n\text{-C}_{15}\text{H}_{32}$ vaporizes at the same time

with water causing the small dip in the vapor profile of $n\text{-C}_{15}\text{H}_{32}$ at Zone 6 when water profile drops to zero instantaneously. Then, profile of $n\text{-C}_{15}\text{H}_{32}$ shows a rapid rise in response to depletion of water in the gas phase and continues to increase, according to K-values, until all of it vaporizes at the time of the second dip.

The second feature is the shape of the production curves in Figure 7-16 which shows that all the liquid is produced during the progression of the two visible evaporation fronts. For all tests performed on Oil A, the cumulative production curves consisted of two parts: a curved line driven by the phase behavior followed by a straight line driven by the viscous forces sweeping the residual out. However, since there is no heavy oil portion in Test 12, all of the produced water and oil are driven by the evaporation mechanism and there is little residual left in the end. The simulation model predicts a 100% oil recovery for Test 12, while the post test experimental analysis shows 0.4 g of residual left on the core. Simulated distillation results for this test (Appendix B) have shown that 96% (by mass) of the produced oil is $n\text{-C}_{15}\text{H}_{32}$ and the remainder consists of lighter and heavier fractions as a result of thermal cracking at higher temperatures. The immobile heavy residual left by the cracking reactions remained on the core to form the unproduced portion of the oil. However, since the cracking reaction was not defined for the nitrogen injection model it could not predict the unproduced residual and gave a 100% recovery. Also post test extractions showed that 0.25 grams of unproduced water was left on the core where the simulation results only showed 0.05 grams as residual water. It was determined that the core used for Test 12 (also Tests 10 to 15) shows 4.81% mass loss on ignition at 600 °C. This indicates the presence of significant amounts of bound water in the core, which was released during decomposition of the core at the temperature range of the second evaporation front in Test 12. This can be the reason for the difference in the amount of the residual water between the experiment and the model.

Or, it can be due to water molecules trapped in the smaller pores that the relative permeability curves could not handle perfectly.

7.3 Simulation of the air injection tests

The verified nitrogen injection model presents a base structure for air injection models, assuring that the distillation and viscous drive mechanisms are modeled adequately. Next, for a practical and meaningful air injection simulation, a meticulously built reaction kinetics model needs to be employed. The procedure of building the reaction kinetics model was as follows:

1. Define a basic common reaction scheme
 - Stoichiometric coefficients calculated through gas phase stoichiometric calculations based on the experimental data
2. Obtain the base values for the kinetic parameters
 - Calculate the activation energy (E) and frequency factor (f) from the experimental data based on the method proposed by Fassihi *et al.* (1984)
 - Calculate the heat of reaction for each reaction based on the amount of fuel burn and oxygen uptake
3. History match the model against the experimental data
 - Fine tuning of the kinetic parameters only allowed for adjustment of the frequency factors since the frequency factors obtained from the experimental methods are not comprehensive
4. Evaluate and study the simulation results and modify the reaction scheme based on scrutinizing the key trends and behaviors observed in the simulation results and also employment of the understandings and analyses made through the course of the experiments.

Step 3 and Step 4 were repeated in cycle until production and temperature histories were satisfactorily reproduced by the model.

7.3.1 Development of the kinetic model

As was previously mentioned, in order to estimate the activation energy and frequency factor of the oxidation/combustion reactions, Fassihi *et al.*'s method was applied to the experimental data of air injection Test 2 (Oil A) and Test 10 ($n\text{-C}_{15}\text{H}_{32}$). The activation energies obtained fell in the common range conceived for the oxygen addition and bond scission reactions in the literature. The activation energy found for the oxygen addition reaction was almost twice as much as that of the bond scission reaction. This was in line with findings of Jia *et al.* (2006) when modeling the low temperature oxidation reactions and their kinetic parameters.

In order to develop the reaction scheme, a simple widely used set of reactions were examined first. This included the liquid phase combustion (bond scission) reactions of the three oil components, i.e. LO, MO, and HO. Also a solid phase residue combustion (known as coke combustion) reaction was built into the scheme. In the literature, generally the heavy oil component is allowed to crack into lighter components and coke. So, initially a 5 reaction scheme including the combustion reactions in the liquid and solid phase and thermal cracking was evaluated. As was expected, the scheme based on the liquid phase combustion reactions failed to reproduce the experimental results of Test 2 precisely. The shape of the exothermic temperature peaks and the formation onset of the combustion front could not be predicted well. Also timings of the formation and consumption of coke were not accurate; thus, the simulated shapes of the leading edge of the oxygen and carbon oxides production profiles were not satisfactory. The amount of the solid residual produced, burnt, and left on the core did not adequately match the experimental data derived from the core ignitions, and the calculated

stoichiometric fuel load during the subsiding part of the produced carbon oxides history. This would call for another source of coke formation. Experimental observations of this study have shown that at temperatures below 350 °C oxygen addition reactions can be active to form a heavy non-volatile (asphaltenes type) liquid component which later cracks to form a solid residue and lighter oil components. Generally the oxygen addition reaction and the oxygen induced cracking reactions are not included in HPAI kinetic modeling. However, including these two reactions in the initial model successfully improved its functionality in terms of matching the onset of combustion front, and profile of coke and product gas.

On the other hand, fine tuning of the newly added vapor phase combustion reactions was a complicated task. The model needed to be enabled to detect when the compositions in the vapor phase fell in the flammable range of the mixture so it could accordingly modify the rates of reactions in the vapor phase. This required using some new keywords in STARS which will be explained in detail in the following subsection (7.3.1.1).

A detailed description of the final reaction scheme and the kinetic parameters for Test 2 are presented in Table 7-2 and Table 7-3. The activation energies, frequency factors, and orders of reaction for the oxygen addition and oxygen induced asphaltenes cracking reactions were adapted from Jia *et al.* (2006). For calculation of the stoichiometric coefficients for these two reactions, insights from the works of Millour (1987) on coke formation delay and Adegbesan (1992) on Asphaltenes solubility were employed. For achieving the optimum stoichiometric coefficients for products of the thermal cracking reaction, the distributions data from the simulated distillation tests of the experimentally produced oils (from Oil A and $n\text{-C}_{15}\text{H}_{32}$ air injection and nitrogen injection tests) were integrated.

Table 7-2: Reaction scheme defined for simulation of Test 2

	Reaction Equation	Phase*
Light Oil Combustion	$\text{LO} + 11.22 \text{ O}_2 \longrightarrow 7.61 \text{ CO}_2 + 7.23 \text{ H}_2\text{O}$	V
Medium Oil Combustion	$\text{MO} + 20.06 \text{ O}_2 \longrightarrow 13.60 \text{ CO}_2 + 12.92 \text{ H}_2\text{O}$	V
Heavy Oil Combustion	$\text{HO} + 44.41 \text{ O}_2 \longrightarrow 30.11 \text{ CO}_2 + 28.6 \text{ H}_2\text{O}$	V
Oxygen Addition	$\text{MO} + 1.005 \text{ O}_2 \longrightarrow 0.37 \text{ Asp}$	L
Oxygen Induced Cracking	$\text{Asp}^{**} \longrightarrow 2.70 \text{ LO} + 0.42 \text{ HO} + 2.77 \text{ O}_2 + 3.95 \text{ Coke}$	L
Thermal Cracking	$\text{Asp} \longrightarrow 1.11 \text{ LO} + 0.54 \text{ HO} + 20 \text{ Coke}$	L
Coke Combustion	$\text{Coke} + 1.25 \text{ O}_2 \longrightarrow \text{CO}_2 + 0.5 \text{ H}_2\text{O}$	S

* V (Vapor), L (Liquid), and S (Solid); ** Asp (Asphaltenes)

Table 7-3: Kinetic parameters for reactions defined in Test 2

	Activation Energy (j/gmol)	Frequency Factor (*)	Enthalpy (j/gmol)	Reaction Order w.r.t. O ₂	Reaction Order w.r.t. HC
Light Oil Combustion	2.3 e4	4.4 e6	4.0 e6	1	1
Medium Oil Combustion	3.6 e4	1.7 e8	7.2 e6	1	1
Heavy Oil Combustion	4.3 e4	7.0 e2	1.2 e7	1	1
Oxygen Addition	7.6 e4	4.0 e3	8.6 e4	1.11	1
Oxygen Induced Cracking	9.4 e4	1.3 e14	0	0.73	2.14
Thermal Cracking	1.0 e5	1.0 e14	0	0	1
Coke Combustion	4.5 e4	1.3 e6	4.1 e5	1	1

* Frequency factor units depend on definition of the reaction rate and other kinetic parameters; hence in lab units frequency factors for reactions 1 to 7 are respectively in these units: (gmol/cm³)⁻¹min⁻¹, (gmol/cm³)⁻¹min⁻¹, (kPa.Min)⁻¹, kPa^{-1.11}min⁻¹, (gmol/cm³)^{-1.14} min⁻¹, min⁻¹, and (gmol/cm³)⁻¹min⁻¹. The appearance of the pressure term in some of the above units is due to dependence of the reaction rate to partial pressure of O₂, where for the rest of reactions it was defined to depend on the molecular concentration of the O₂.

7.3.1.1 Vapor phase reaction kinetics

A proper equation for the reaction rate of a vapor phase combustion reaction must comply with the flammability range of the mixture of fuel and oxidant within that phase.

This calls for a model that can instantaneously

1. calculate the ratio of air/oxygen to fuel in the vapor phase
2. recognize where the air/oxygen to fuel ratio falls in the flammability range of the vapor mixture
3. modify the reaction rate accordingly to meet the rate requirements of a fuel lean/rich or stoichiometric mixture

Section 5.2.1 in Chapter 5 provided details on the concept and applications of flammability range. It described how the flammability range of the mixture depends on temperature and pressure. It was also mentioned that due to the non-uniformity of this dependence and also the complexity of the concept and lack of enough data in the literature, the flammability envelope of a complex mixture (such as what is dealt with in the air injection process), cannot be simply measured nor calculated. Therefore, for the purpose of the definitions of the flammability limits, it was needed to rely on the:

1. trends obtained from the experimental data; i.e. associating the formation and development of the visible combustion front with the concentration of the fuel and oxygen in the vapor phase and looking for the lean side and rich side of the flammable range
2. simplified tables from the literature where the flammability limits for different mixtures of oxygen and pure hydrocarbons are listed (Rose and Cooper, 1977)
3. integration of lean and rich limits into the simulation model and refinement of the model against the experimental data (especially the temperature and product gas profiles) of the air injection tests

Since the STARS software is not designed to directly recognize the flammable range and apply fuel lean and rich limits for reaction rate calculations, use was made of the existing keywords in a manner that they could superimpose the concepts of the lean and rich limit to the model and adjust the rate equations consequently. It would be optimal if a new kinetics package was written and added to the existing STARS kinetic model to meticulously follow the mixture concentration in the vapor phase and modify the reaction rates directly based on a predefined procedure. Ideally the reaction rate should be zero outside of the flammable range, reach maximum at the stoichiometric air/fuel concentration ratio and decrease towards the lean and rich limits. These effects were satisfactorily induced by employment of two keywords in STARS: RXEQFOR, and RXCMPFAC.

RXEQFOR modifies the reaction expression for the specified component in that the deviation from equilibrium mole fraction is employed. Thus, the concentration factor for the component in a particular phase (indicated here as subscript i) becomes $C_i = \phi \rho_i S_i \Delta x_i$; where $\Delta x_i = \max(0, x_i - x_{equilibrium})$. This keyword was used for setting a reaction rate of zero to a component when it's concentration in the vapor phase fell below the lean limit. Also it was used to eliminate the cracking of asphaltenes before it reached its equilibrium solubility limit.

RXCMPFAC enables the reaction rate to be divided by a factor of $(1 + x)^B$ where x is the component's mole fraction in an indicated phase. This keyword was used to decrease the rate of reaction when the concentration of the mixture fell towards the rich limit. It would be ideal to incorporate a logarithmic correlation so the reaction rate could be zero once the mixture moved out of the flammable range and into the fuel rich zone. However, the power correlation was the only option available in STARS and the

temperature results, as will be reviewed later, were not the optimal representation of the experiments on the fuel rich side of the flammability envelope.

Defining the lean and rich limits for the LO, MO, and HO components was initially based on the trends identified from the experimental results. It was learned that in the HPRT0 tests, the vapor phase fuel concentration changes from lean to stoichiometric to rich. However the lean and rich concentration values for each oil component in the vapor phase needed to be defined for the model. Although the stoichiometric air/fuel ratios at standard conditions are known, there is no data on the exact values at the temperature and pressure conditions of the HPRT0 tests. Therefore, initially the lean and rich limits were defined based on the vapor phase concentrations of the fuel components in the nitrogen injection model. Then, these limits were refined by tuning the temperature results of the air injection simulation model to the temperature profile obtained from air injection Test 2. The complication of this procedure was imposed by the fact that the overall flammable range of a mixture which affects the temperatures depends on the total fuel in the vapor phase, i.e. the sum of x_{LO} , x_{MO} , and x_{HO} . However, using the STARS software the limits for each component were to be set individually for that particular component due to STARS's limitations. However the following strategy was employed to overcome the problem:

First, based on the experimental data, the flammability range was assumed and lean and rich limit concentration values for each component were set. The simulation model was then run and the concentration profiles in the vapor phase for each component were derived. If the total concentration of the fuel components (i.e. the sum of x_{LO} , x_{MO} , and x_{HO}) fell in either lean, rich, or stoichiometric region that was assumed based on the experimental results, and also if the shapes of the temperature peaks reflected the behavior expected within that particular region; then, the flammability limits were

considered as verified. This procedure proved to be successful, mostly due to close to accurate initial trials- owing to the insights from the experimental study.

Rose and Cooper (1977) tabulated the theoretical (or stoichiometric) combustion requirements of the gases concerned in the combustion of fuels. Based on the molar air/fuel values reported in their book for the pure components up to $C_{10}H_{22}$ and also the observation that these values trended on a logarithmic curve, it can be assumed that for the light Oil A (with a composition distribution mostly comprised around $n-C_{15}H_{32}$) a fuel molar fraction between 0.002 and 0.02 may fall into the near stoichiometric region depending on the temperature and the consequent fuel composition in the vapor phase. The air/fuel ratios obtained from simulation of Test 2 will be reported along with the rest of the simulation results.

7.3.2 Air injection Test 2

Figures 7-18, 7-19 and 7-20 present the simulation results for high flux air injection Test 2. Figure 7-18 shows the temperature history along with the profiles of LO, asphaltenes, and coke components in the first active upstream zone (Zone 2). The formation onset of the visible thermal front was successfully predicted by the kinetic and phase behavior models. The ignition delay corresponds to the time needed for oxygen addition and oxygen induced cracking reactions to generate compounds in the gas phase. It was observed in the simulation results of the nitrogen injection Test 1 (Figure 7-8) that all the LO in each zone was evaporated before both a visible evaporation front and a thermal front reached at that particular zone. Also the profile of LO in Figure 7-18 shows that the original LO in Zone 2 is evaporated before the 100th minute into the run. However there is a second peak for LO in the gas phase which coincides with formation of coke and cracking of asphaltenes as indicated by the profiles of these components. This shows the activation of the oxygen induced cracking reaction which consumes the asphaltenes

to generate LO, HO, and coke. Now, generation of the cracked LO component in Zone 2 occurs together with the appearance of the thermal front in that zone. This indicates that the kinetic model has been able to satisfactorily predict the onset and rate of the oxygen addition and oxygen induced cracking reactions and also the phase behavior model has fed the right amount of LO and MO to the gas phase for the fuel to fall in the flammable range (from the lean side) and ignite the thermal front.

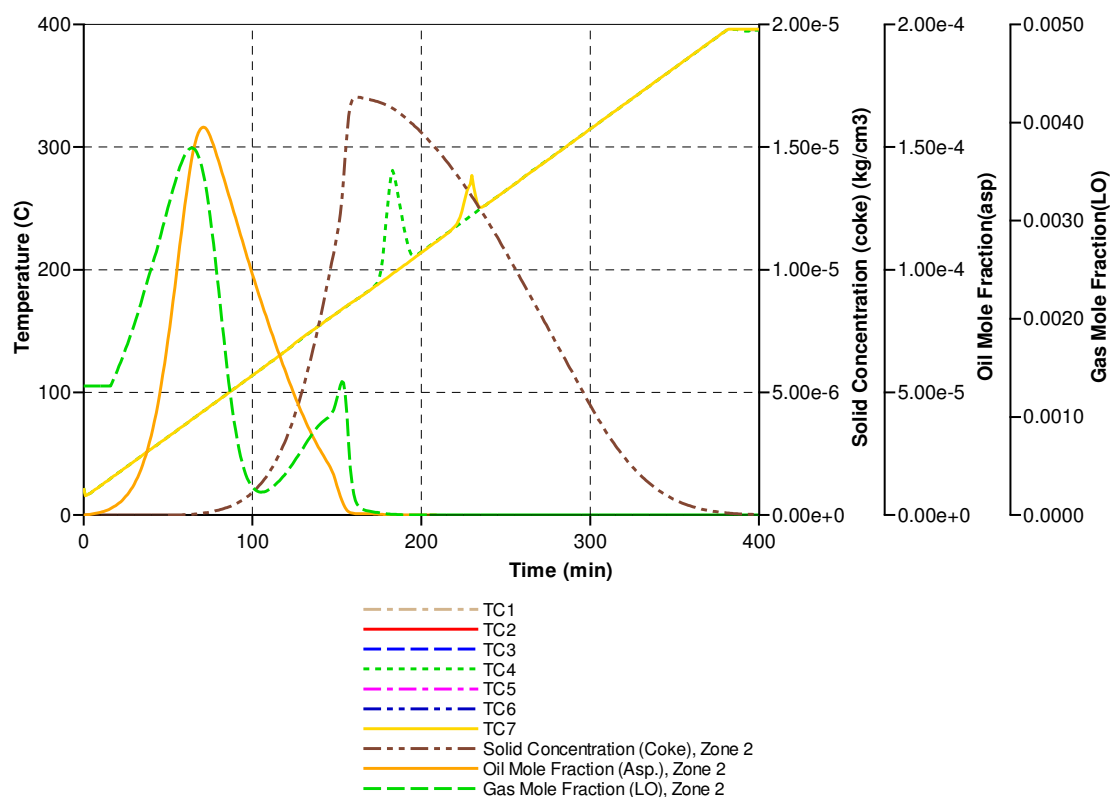


Figure 7-18: Temperature history and profiles of LO, asphaltenes, and coke components in the first active upstream zone (Zone 2), as modeled for air injection Test 2 (Oil A, air, 38.2 sm³/m²h)

In Figure 7-18 the generated coke in Zone 2, although very small in absolute amount, takes almost 4 hours to totally burn. This is in line with the observations from the experimental results, where the profile of product oxygen had a very low build up rate. The simulated product gas composition in Figure 7-19 also shows the slow rise in oxygen and decline in carbon oxides profiles. The drop in the oxygen concentration during the ignition delay time represents the oxygen consumed by the oxygen addition reactions.

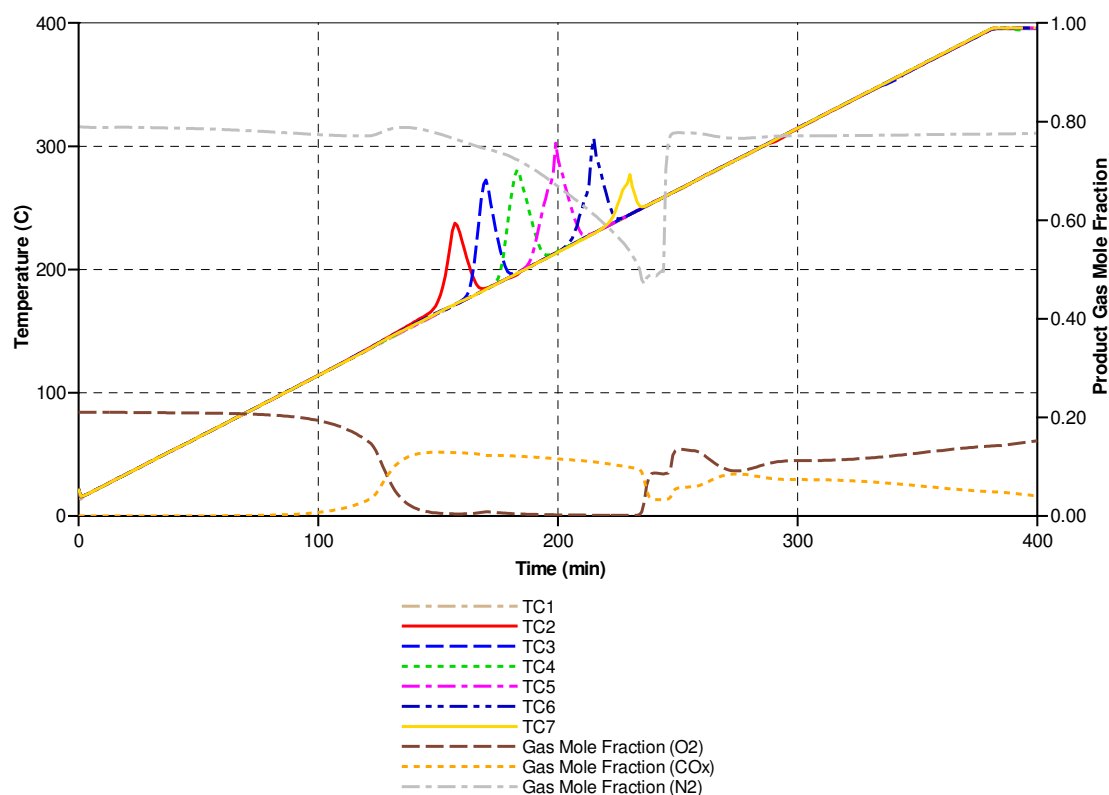


Figure 7-19: Product gas composition and temperature history as modeled for air injection Test 2 (Oil A, air, 38.2 sm³/m²h)

It can be noted in Figure 7-19 that composition of nitrogen gradually declines as the thermal front advances inside the reactor. This is due to gradual vaporization of the original and the produced water since the compositions shown in this figure are those calculated in the last cell inside the reactor, before the water vapor condenses and is produced. So as the water vapor increases with time and temperature, mole fraction of nitrogen decreases in the gas phase until all the producible water is vaporised and removed.

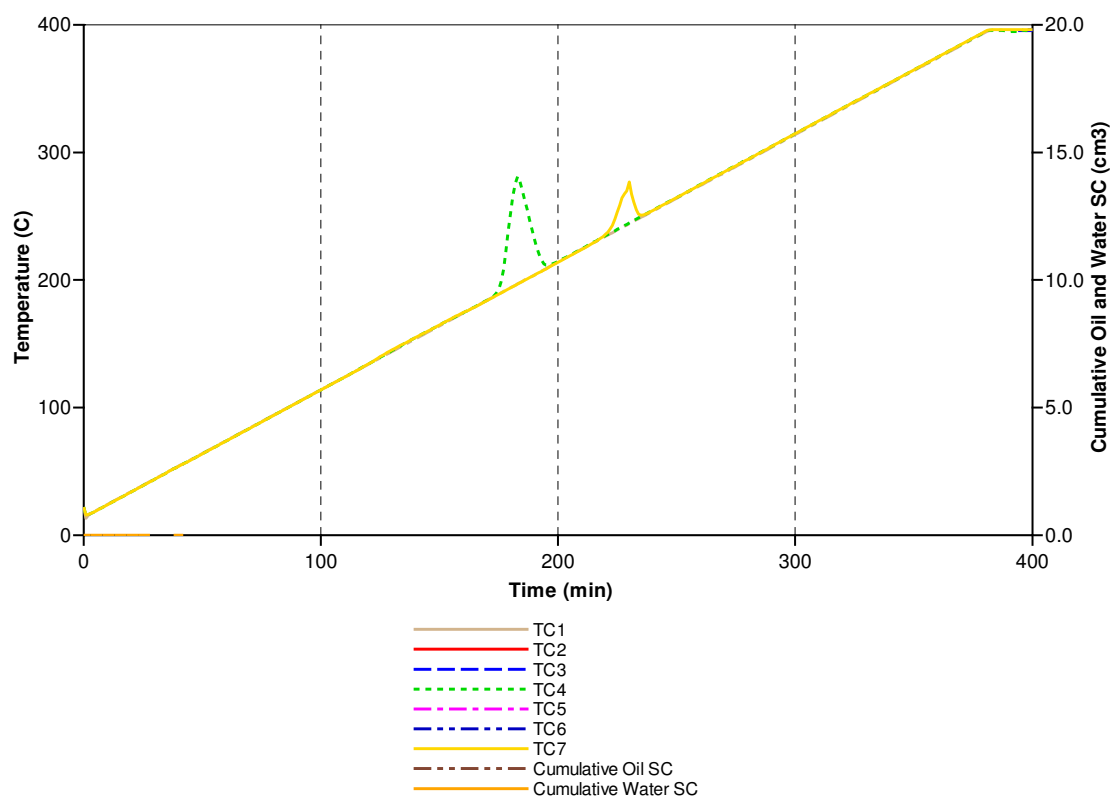


Figure 7-20: Temperature history and cumulative liquid production as modeled for Test 2 (Oil A, air, 38.2 sm³/m²h)

Figure 7-20 plots the cumulative oil and water production at standard conditions up to the 400th minute of the runtime. The total simulated oil and water produced from Test 2 were 8.18 g and 17.54 g respectively. The experimental values for these parameters were 8.6 g and 9.25 g in the same order (Table 4-2). Since the experimental production data for Test 2 were not accurate due to deficiency of the primary production traps and considerable amounts of water were lost during the production, a comparison between the simulated and experimental water production data for this particular test cannot be made. It can be noted that the major fraction of water, which also includes the generated water, is produced during the advancement of the reaction front. Also the rate of oil production during this period is twice the production rate after passage of the thermal front. This is reflective of the incremental oil produced by thermal drive in addition to the viscous and evaporation drive mechanisms. The total duration for advancement of the thermal front in the simulation profile was 100 minutes where the experimental value was 110 minutes (Figure 4-3). This difference between the experimental and simulated front velocities is considered as acceptable since the task of the kinetic model involves modification of the rates for 7 reactions, each of which imposing their own complications to STARS such as lean limit, rich limit, or solubility limit.

Table 7-4 to 7-9 present the amount of hydrocarbon fuel (sum of LO, MO, and HO) and oxygen in the gas phase for each of the zones during the time they go through the rapid temperature rise set off by passage of the thermal front. The oxygen/fuel and air/fuel values are reported accordingly.

As was mentioned previously, if a fuel mole fraction between 0.002 and 0.02 is considered to be in the flammable region, then according to the tabulated values Zone 4, Zone 5, and Zone 6 are on the rich side for the second half of the combustion period and Zone 7 is on the rich side for the whole combustion period. However, the calculated

values indicate that the last value for the fuel mole fraction in Zones 5 and 6 drops to a stoichiometric level and this is reflected by the shape of the temperature peaks at these zones. Figure 7-18 shows that while the slope of temperature rises at both Zones 5 and 6 seems to decrease with time, there's a sudden sharp rise as the peak temperatures are approached. Zone 7 reflects its richness with much smaller peak size compared to the rest of the zones. Another useful finding from the air/fuel ratios in these tables is that the rich side of the flammable range can extend significantly at high pressures, while the effect of pressure on the lean side is minimal. Zone 2, starting on the lean limit, exhibits air/fuel numbers close to values expected at standard conditions.

Table 7-4: Oxygen and fuel data in the gas phase as simulated for Zone 2 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
144	163	0.139	0.003	0.56	5.86	27.59
145	164	0.137	0.003	0.58	5.59	26.34
146	166	0.134	0.003	0.60	5.27	24.82
147	168	0.131	0.003	0.63	4.89	23.04
148	171	0.127	0.004	0.67	4.46	21.01
149	174	0.121	0.004	0.72	3.98	18.75
150	179	0.115	0.004	0.79	3.42	16.13
151	184	0.107	0.005	0.88	2.87	13.50
152	191	0.098	0.005	0.97	2.40	11.31
153	200	0.091	0.005	1.01	2.14	10.08
154	209	0.088	0.005	0.94	2.20	10.38
155	219	0.093	0.004	0.77	2.86	13.49
156	228	0.105	0.003	0.55	4.55	21.45
157	233	0.121	0.002	0.36	7.91	37.27

Table 7-5: Oxygen and fuel data in the gas phase as simulated for Zone 3 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
160	176	0.020	0.005	0.90	0.53	2.52
161	178	0.019	0.006	0.95	0.47	2.21
162	182	0.017	0.006	1.05	0.39	1.84
163	190	0.016	0.007	1.29	0.30	1.42
164	202	0.016	0.009	1.75	0.22	1.04
165	219	0.019	0.013	2.52	0.17	0.82
166	238	0.025	0.017	3.51	0.17	0.80
167	257	0.042	0.019	3.97	0.25	1.19
168	270	0.074	0.014	3.05	0.58	2.72
169	274	0.106	0.006	1.61	1.56	7.33

Table 7-6: Oxygen and fuel data in the gas phase as simulated for Zone 4 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
174	194	0.003	0.009	1.54	0.04	0.21
175	203	0.003	0.010	1.89	0.04	0.17
176	216	0.003	0.013	2.57	0.03	0.14
177	232	0.004	0.018	3.65	0.03	0.13
178	249	0.006	0.025	5.01	0.03	0.13
179	263	0.010	0.029	6.13	0.04	0.19
180	274	0.021	0.029	6.17	0.08	0.37
181	281	0.047	0.021	4.60	0.24	1.13
182	284	0.116	0.010	2.51	1.09	5.12
183	299	0.152	0.007	2.30	1.56	7.36

Table 7-7: Oxygen and fuel data in the gas phase as simulated for Zone 5 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
186	203	0.001	0.010	1.82	0.01	0.03
187	205	0.001	0.010	1.95	0.01	0.04
188	211	0.001	0.012	2.22	0.01	0.04
189	218	0.001	0.013	2.64	0.01	0.04
190	228	0.001	0.017	3.33	0.01	0.03
191	237	0.002	0.020	4.10	0.01	0.05
192	250	0.002	0.025	5.26	0.01	0.05
193	257	0.003	0.029	6.01	0.01	0.06
194	268	0.007	0.034	7.06	0.02	0.11
195	271	0.021	0.032	6.70	0.07	0.34
196	280	0.079	0.027	5.79	0.32	1.52
197	315	0.138	0.023	5.48	0.60	2.80
198	334	0.153	0.009	2.68	1.35	6.35

Table 7-8: Oxygen and fuel data in the gas phase as simulated for Zone 6 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
203	220	0.000	0.013	2.56	0.00	0.01
204	222	0.000	0.014	2.74	0.00	0.01
205	225	0.000	0.015	2.98	0.00	0.01
206	230	0.001	0.017	3.38	0.00	0.02
207	235	0.001	0.019	3.78	0.00	0.02
208	240	0.001	0.021	4.31	0.00	0.02
209	246	0.001	0.024	4.85	0.01	0.02
210	251	0.001	0.026	5.37	0.01	0.03
211	257	0.003	0.029	6.04	0.01	0.05
212	260	0.006	0.030	6.24	0.02	0.11
213	266	0.015	0.031	6.42	0.06	0.26
214	292	0.080	0.044	9.46	0.20	0.94
215	333	0.154	0.029	6.62	0.55	2.58
216	355	0.170	0.011	3.03	1.32	6.24

Table 7-9: Oxygen and fuel data in the gas phase as simulated for Zone 7 during the passage of the thermal front in Test 2 (Oil A, air, 38.2 sm³/m²h)

Time (min)	Temperature (°C)	Oxygen Mole Fraction	Fuel Mole Fraction	Fuel (g)	Oxygen/Fuel (sm ³ /kg)	Air/Fuel (sm ³ /kg)
226	246	0.001	0.022	4.62	0.00	0.02
227	250	0.001	0.024	5.00	0.00	0.02
228	254	0.002	0.026	5.43	0.01	0.03
229	259	0.004	0.028	5.90	0.02	0.07
230	261	0.010	0.028	5.79	0.04	0.20
231	269	0.042	0.025	5.41	0.18	0.86
232	308	0.126	0.028	6.49	0.46	2.16
233	339	0.157	0.012	3.18	1.17	5.49

7.3.3 Air injection Test 10

In order to evaluate the proposed kinetic model it was employed to simulate the air injection Test 10 on pure n-C₁₅H₃₂. Since the progression of the oxygen addition reactions is dependent on the type and composition of the oil undergoing this reaction, simulation of Test 10 required a set of oxygen addition and oxygen induced cracking reactions with modified stoichiometric coefficients accordingly to compensate for the composition difference between light Oil A and the pure component. Table 7-10 lists these two reactions. Experimental oxygen utilization data and produced oil's simulated distillation data were incorporated into modification of the stoichiometric coefficients.

Table 7-10: Oxygen addition and oxygen induced reaction scheme for Test 10

Oxygen Addition	MO + 10.00 O ₂ → 0.84 Asp
Oxygen Induced Cracking	Asp → 1.88 LO + 0.03 HO + 1.72 O ₂ + 11.79 Coke

Figure 7-21 presents the temperature history and product gas compositions for Test 10. The produced gas profiles feature the same trends as Test 2 as expected from the experimental results of Test 10 (Figure 4-21). Interestingly, the shape of the first temperature peak, with a very steep leading edge slope, matches the exact shape of experimental Zone 2. Unlike Test 2, formation of the thermal front in Test 10 (owing to excessive amounts of medium oil or $n\text{-C}_{15}\text{H}_{32}$) starts near the stoichiometric region which is reflected by the sharp first peak. However, similar to modeling of Test 2, the richness of the fuel which happens later and causes a lower rate and rounder peak shapes could not be captured perfectly with the current kinetic model. Nevertheless, the clipped off shape of the peaks in the first few Zones indicates that the model is detecting the richness of the fuel and lowers the combustion reaction rate but is unfortunately not capable to replicate the exact shape of the peaks.

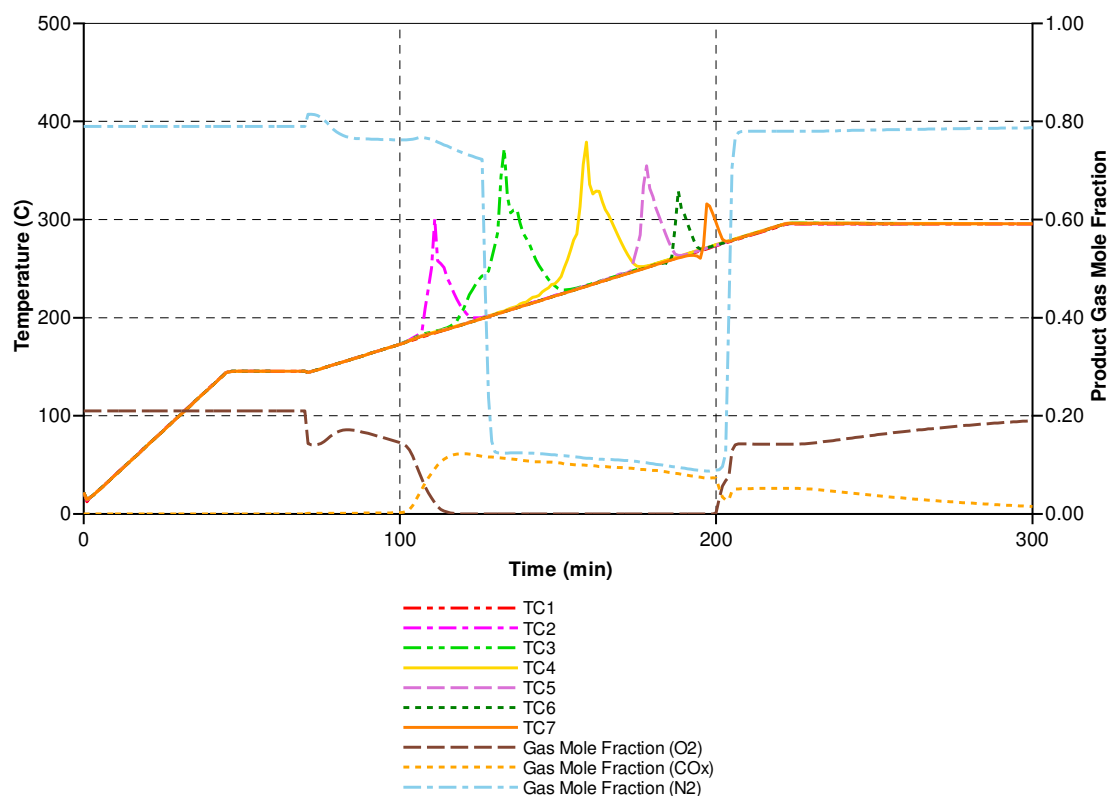


Figure 7-21: Temperature history and product gas composition as modeled for Test 10 ($n\text{-C}_{15}\text{H}_{32}$, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

Liquid productions in Figure 7-22 show a total of 7.23 g and 13.05 g for produced oil and water respectively. These numbers are in agreement with the experimental values of 7.19 g for the collected oil and 10.89 g for the collected water. There's a 15% difference between the simulated and experimental water production. The kinetic model seems to be imposing production of more water. This indicates that the rate of the water-generating combustion reactions are not perfectly adjusted against the rate of oxygen addition reactions and more oxygen is predicted to be burned into water.

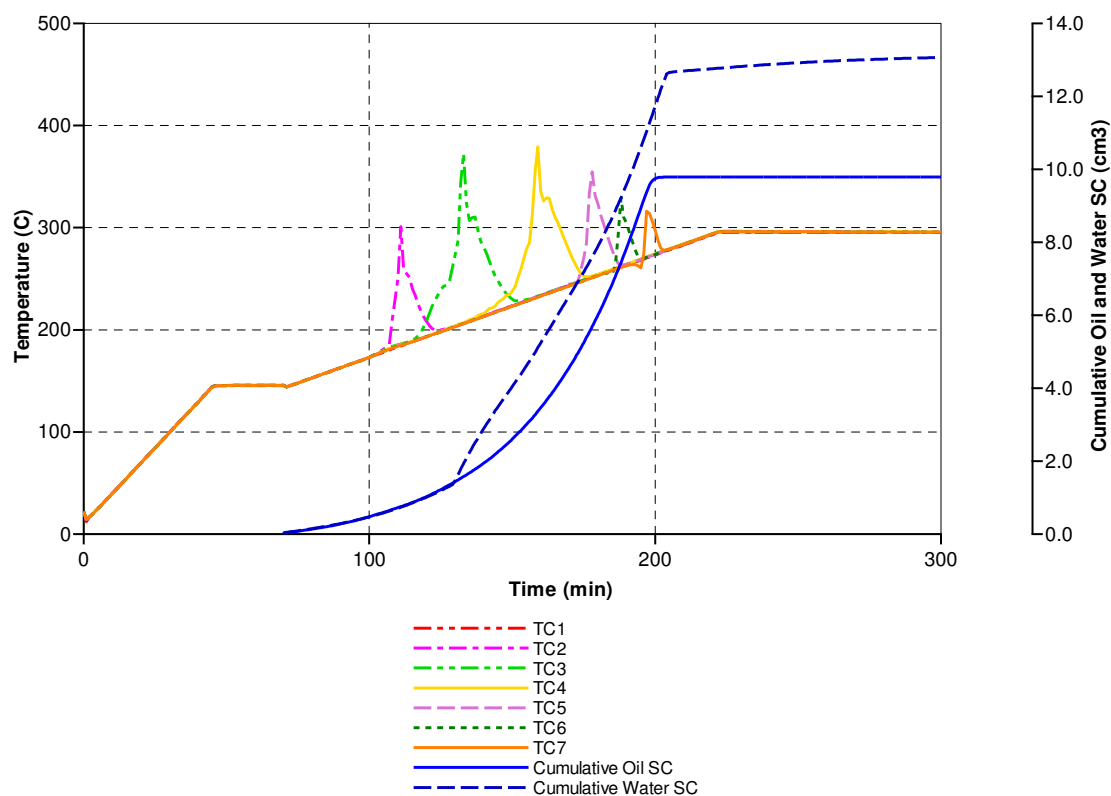


Figure 7-22: Temperature history and cumulative liquid production as modeled for Test 10 ($n\text{-C}_{15}\text{H}_{32}$, air, $38.2 \text{ sm}^3/\text{m}^2\text{h}$)

7.3.4 Air injection Test 15

The low flux air injection Test 15 on Oil A was simulated with the proposed kinetic model. It is noticed in Figure 7-23 that except for the first active zone (Zone 2), all the MO is stripped from the individual zones before the thermal front arrives at those zones. On the other hand, Figure 7-24 exhibits how each temperature peak associates with consumption of all the HO from both liquid and vapor phases. It was also known from the experimental data (Figure 4-17) that when the thermal front extends up to 400°C , it is burning on HO component. Thus a liquid phase HO combustion reaction was allowed for the low flux Test 15 with a frequency factor of $1.2 (\text{kPa Min})^{-1}$. Also the rate of HO

combustion in the vapor phase was modified with a frequency factor of $1009 \text{ (kPa Min)}^{-1}$. Figure 7-24 highlights the involvement of HO from both liquid and vapor phases in the combustion reactions.

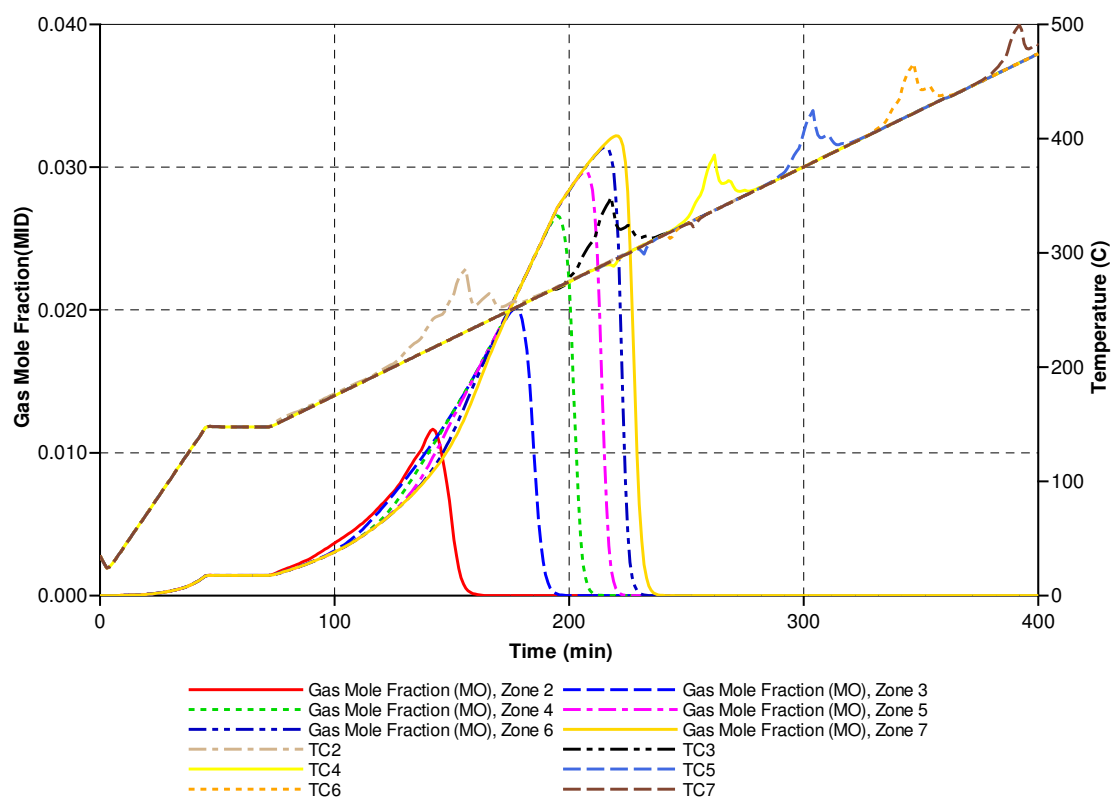


Figure 7-23 Temperature history and MO gas mole fractions as modeled for Test 15 (Oil A, air, $12.75 \text{ sm}^3/\text{m}^2\text{h}$)

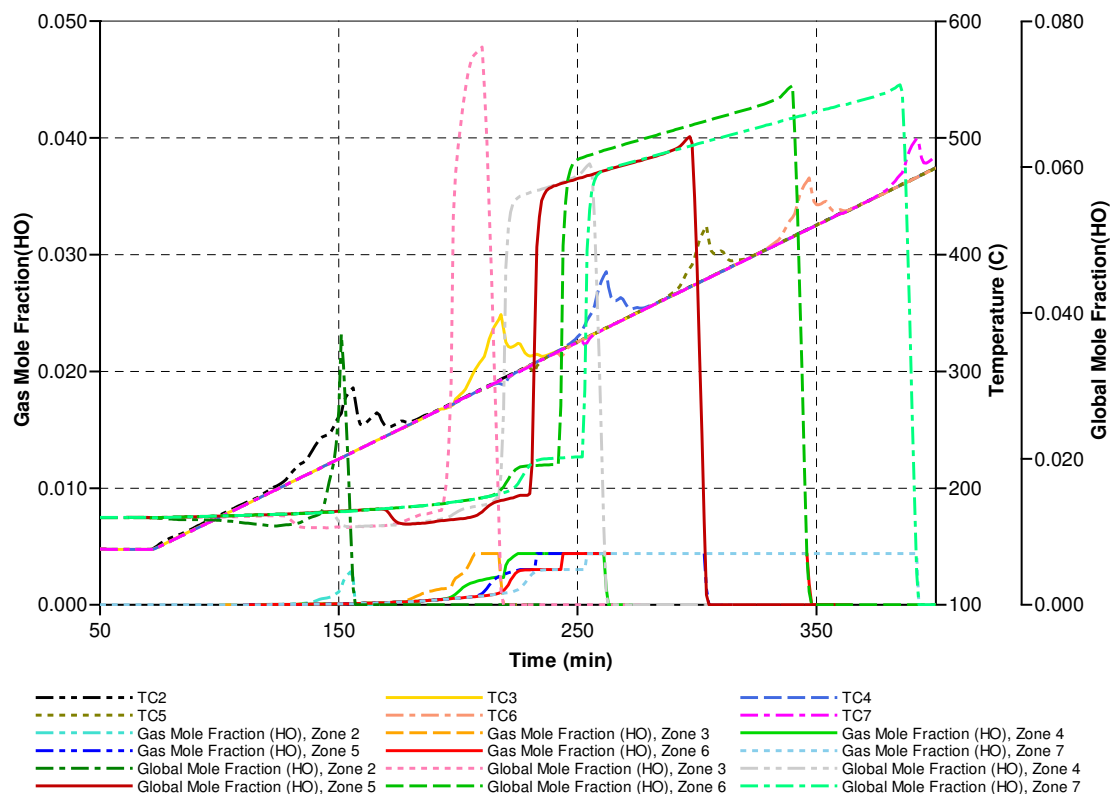


Figure 7-24: Temperature history along with HO gas mole fractions and global mole fractions as modelled for Test 15 (Oil A, air, 12.75 sm³/m²h)

The product gas compositions are plotted in Figure 7-25 with regard to temperature history of Test 15. The distinct evaporation front that was observed in the experimental results of this test could be captured by the simulation model. The interesting feature about the evaporation front is its coincidence with the decline in the N₂ profile. As was observed for the other tests, nitrogen and carbon oxides molar fractions decrease as water vapor increases in the vapor phase.

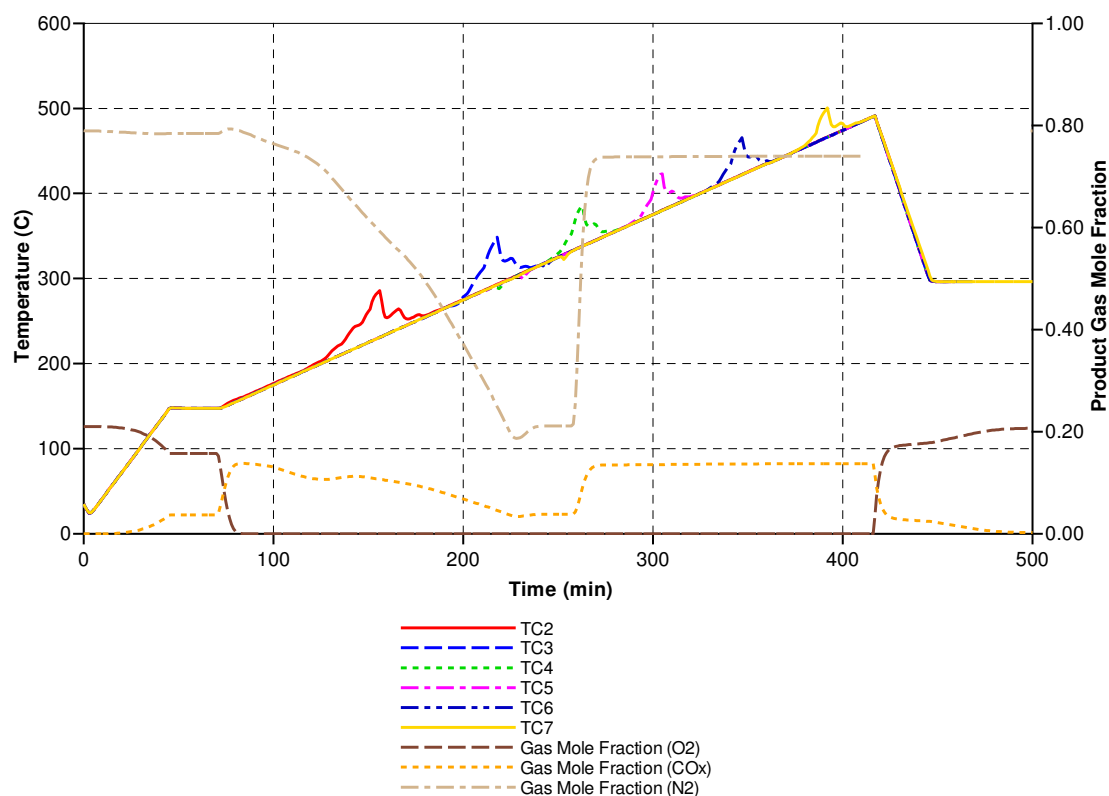


Figure 7-25: Temperature history and product gas composition as modeled for Test 15 (Oil A, air, 12.75 sm³/m²h)

Similar to the experimental data, the temperature peaks become narrower as the thermal front proceeds inside the reactor. Figure 7-26 shows a cumulative oil production of 6.83 g and water production of 14.07 g. The experimental values were 6.34 g and 11.50 g for oil and water respectively. Similar to Test 10, the higher prediction of water is due to utilization of more oxygen by the combustion reactions and less oxygen by the oxygen addition reactions.

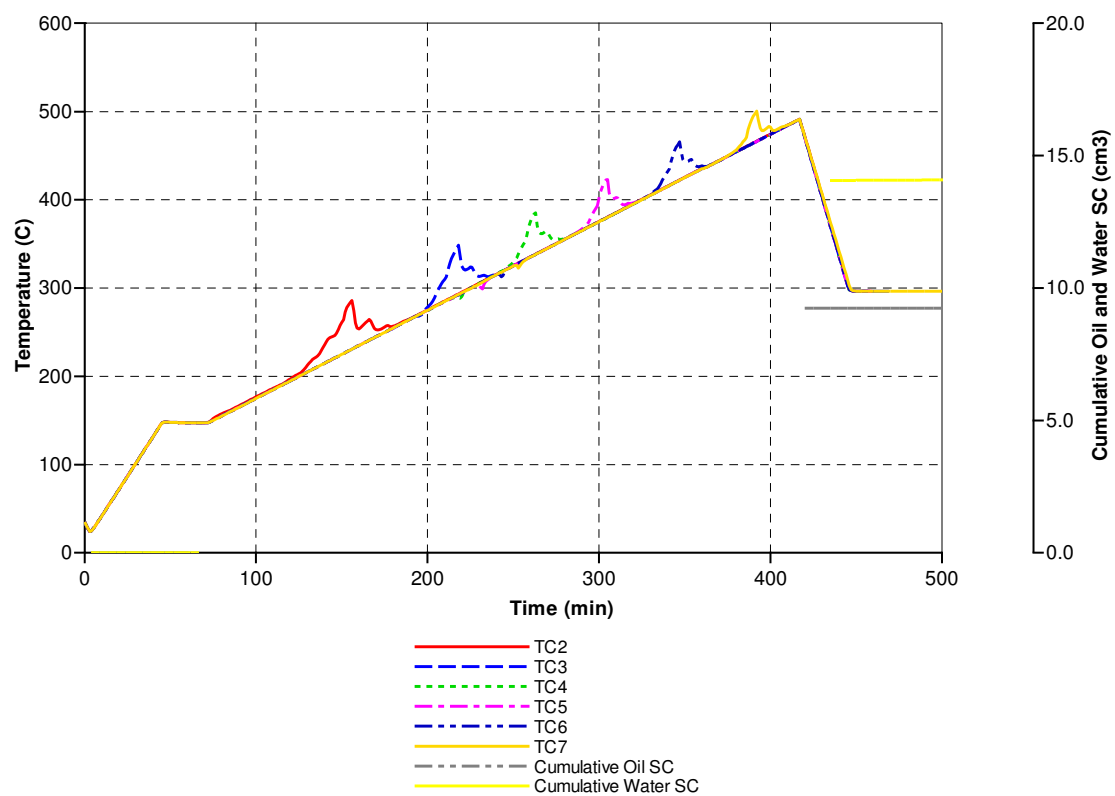


Figure 7-26: Temperature history and cumulative Liquid Production for Test 15
(Oil A, air, 12.75 sm³/m²h)

Chapter Eight: Summary, Conclusion, and Recommendations

8.1 Summary

In this dissertation a kinetics model for the chemical reactions occurring under high pressure air injection was developed through both experimental study and numerical simulation. The methodology included:

- The design of a high pressure RTO reactor for representation of the HPAI reservoir conditions in the laboratory while performing various air injection and nitrogen injection tests. The experiments were conducted on either the selected light oil or the pure hydrocarbon component in both the presence and absence of interstitial water. Two heating processes were applied: isothermal (at reservoir temperature) and ramped temperature modes. Two injection flux levels of “high” and “low” were examined.
- Analysis of the temperature history and liquid production from the nitrogen injection tests to study the distillation behavior and characterize the evaporation drive mechanism and its potential associations with the reaction kinetics.
- Study of the effect of mass transfer under different injection fluxes to determine whether mass transfer was a rate-controlling mechanism during activation of the chemical reactions under the conditions of the HPRTTO tests.
- Investigation of the impact of interstitial water in the HPAI process
- Scrutinizing the progress of the evaporation and combustion fronts inside the reactor during the experiments by calculation of their advancement velocity which is directly linked to the air requirement. This also enabled verification of how both mechanisms of evaporation and combustion chronologically develop relative to each other and whether vapor phase reactions were possible.

- Analysis of the product gas composition of the air injection tests and calculation of the combustion gas phase parameters (e.g. H/C and air/fuel ratios) to get an insight into the fate of hydrogen, carbon and oxygen atoms during the oxidation/combustion reactions. Also to look for the trends over which these parameters vary in order to correlate them with the kinetics path.
- Conducting simulated distillation tests on the produced oils from all tests to measure the distribution of the single carbon number groups which signifies how the evaporation mechanism and also the cracking reactions affect the composition of the produced oil. The findings were later incorporated into the stoichiometric coefficients of the reaction equations.
- Building a comprehensive equation of state phase behavior model, using data generated through several PVT tests.
- Development of a methodology, using the phase behavior model, to obtain fully compositional K-values under the HPRT0 test conditions to employ in the numerical simulation model.
- Study of the potential flammability range of the selected oil under the injection flux of the HPRT0 tests based on the air and fuel compositions obtained utilizing the proposed fully compositional K-values.
- Evaluating whether the widely used non compositional K-values are suitable for use in HPAI numerical simulations.
- Building a comprehensive thermal numerical simulation model to replicate the HPAI process under the HPRT0 test conditions.
- Development of the reaction schemes and kinetic parameters for light Oil A based on all the data, information and comprehensions achieved during the course of this study.
- Verification of the kinetic model.

8.2 Concluding Remarks

In the light of the experimental and numerical studies conducted for the purpose of this research, a comprehensive kinetic model was developed for light oils undergoing HPAI. Based on the findings of this study, during HPAI, combustion reactions can be active in the vapor phase when the composition of the mixture of the fuel and oxygen in the vapor phase falls in the flammable region of the mixture. Vapor phase combustion reactions and their flammability limits were integrated into the proposed kinetic model.

Main results of this study can be summarized as:

1. Distillation or evaporation/condensation of the components in HPAI is a major controlling mechanism that directly impacts the kinetics of the combustion reactions. It not only acts as a drive mechanism but moreover feeds the vapor phase combustion reactions with at least part of the fuel; provided that the composition of the vapor phase is within the flammable range.
2. HPAI is a thermal process rather than a flue gas injection method. The isothermal nitrogen injection test resulted in merely 18% oil recovery. But, air injection tests under HPRTD conditions produced at least 60% of the original oil.
3. In the high pressure ramped temperature tests performed for the purpose of this study, distillation was dominated by the phase behavior and was not mass transfer limited.
4. The experimental part of this research concentrated on four operating parameters: oil composition, injection gas composition (air or nitrogen), injection gas flux, and initial water saturation. The resulting temperature profiles showed that these four parameters impact the formation, shape and the propagation velocity of the endothermic evaporation front and the exothermic oxidation/combustion front in nitrogen injection and air injection tests.

5. Oxygen addition reactions are active during the propagation of the exothermic combustion wave over the temperature ranges observed in the reported tests; i.e. below 300 °C.
6. Ignition is triggered by the heat generated through oxygen addition reactions and the gas phase light components generated by oxygen induced cracking of the products of oxygen addition reactions. Prior to the formation of the thermal front, composition of the fuel in the vapor phase is lean and thus addition of the cracking products contributes to the flammability of the mixture.
7. Over the temperature range where combustion reactions occurred in the vapor phase, the presence of connate water increases the richness of the fuel in the vapor phase by diluting the oxygen concentration.
8. For the conditions of the reported air injection tests, oxygen break through occurs as the combustion zone approaches the outlet of the core. The vapor phase is expected to approach a fuel-rich condition which causes the termination of the vapor phase combustion reactions. Once the homogeneous vapor phase combustion wave is no longer present, heterogeneous combustion reactions involving residue remaining after passage of the vapor phase combustion wave are evident by the slow build up of oxygen in the product gas phase. The lower oxygen uptake rate during this period suggests that the reactions are mass transfer-controlled.
9. Compositional K-values developed in this study were compared to correlation based K-values. A considerable overestimation of K-values was observed from the widely used Wilson correlation.

8.3 Recommendations:

In order to generate realistic predictions from numerical simulation models for HPAI, certain aspects of the process need inclusive characterizations prior to incorporation into the simulation model. Namely, reaction kinetic and phase behavior models that have been addressed in this dissertation.

It is believed that distillation is a controlling mechanism associated with the kinetics of oxidation/combustion reactions in HPAI. Comprehensive phase behavior studies are needed as preliminary work to characterize the distillation behavior of oils in the presence of water at the temperatures and pressures which will be experienced in the field process.

Vapor phase combustion has a key role in the kinetics of HPAI and participation of oil components in the vapor phase in oxidation/combustion reactions should be included in the kinetics of HPAI. In order to do this, the simulation model must be able to predict whether the vapor phase is in the flammable range at the operating pressure, since the composition of the hydrocarbon in the vapor phase is a very important factor in terms of defining the rate of reactions, hence the kinetics of the vapor phase combustion. A multi-phase compositional phase behavior model is useful for determining the vapor phase compositions as a function of initial oil composition, water concentration, air flux, pressure, and temperature. Moreover, the effects of thermal and oxygen induced cracking reactions, in terms of their contribution to the generation of hydrocarbon fractions should be accounted for when building a meaningful kinetics model.

For future research work in this area the following are recommended:

- There is still room for improvement of the experimental set-up designed and used for this study, in particular to the liquid collection system

- Attempts were made to set the collector vessel on a digital scale, so that the amount of produced liquid could be measured with time. However, the thermal stress imposed to the production lines did not allow for correct recordings of the weight. Blocking the thermal stress and enabling the instantaneous weight measurements will contribute to provide a detailed liquid production profile which is helpful for improvement of the simulation model.
- A collector vessel constructed from high pressure sight glass is recommended since it enables recordings of the type and sequence of the produced fluids.
- Calibration of the mass flow meter prior to every single experiment is recommended, especially after very long test durations or when switching between injection gases. Fortunately the level of precision of the mass flow meter for the undertaken experimental study was tolerable, but care must be taken when the tests are flux-sensitive.
- The reactor was pressurized with helium prior to initiation of the tests. Once the desired pressure and temperature was reached, air injection was started. Helium was chosen over oxygen in this research since investigation of the oxygen addition reactions and consequently the time period and temperature history over which the oil was exposed to oxygen were of particular importance. This was achieved with the cost of losing the initial GC readings when helium was being displaced out of the reactor. If the type of the research is not highly sensitive to the onset of the oxygen addition reactions, it is recommended that the reactor is pressurized with air.
- There's much latitude for improvement of the current commercially available thermal numerical simulation packages in order to better replicate the HPAI process.

- CMG WinProp phase behavior software is capable of performing compositional multi phase flashes to obtain K-values. However the thermal software CMG STARS is limited in terms of choosing the methods that provide K-values. Apart from the non-compositional options, there's only one semi-compositional option in which the user can define a key component in order for the software to generate K-values in accordance with that particular component's composition. Findings of this research have shown that the kinetics of reactions in HPAI are highly sensitive to the composition in the vapor phase and thus encourage use of the most accurate K-values. Therefore, it is recommended that STARS is reformulated and modified to employ instantaneous multi phase compositional K-values generated by WinProp.
- Defining the lean and rich limits for the composition of fuel in the vapor phase and adjusting the rate of vapor phase reactions in accordance with the placement of the mixture composition within its flammability envelope was a complex procedure. It is recommended that for the purpose of HPAI simulations, the thermal modeling software integrate the concept of the flammability range into their packages. This will require the model to instantaneously evaluate whether the summation of all available hydrocarbon fuel compositions in the vapor phase falls in the predefined flammable range. Provided the answer to this "if statement" is positive, vapor phase combustion reactions may be activated. In order to decrease the rate of combustion when the composition of fuel moves away from near stoichiometric condition and towards the lean and rich limits, a predefined logarithmic correlation between rate and fuel composition is helpful. The user may define the parameters to this correlation according to the particular characteristics of the individual oils. It need not be mentioned that for a successful application of HPAI to a field, experimental phase behavior and

kinetics study on the mixture of the reservoir's oil, water and core under the reservoir conditions is the key.

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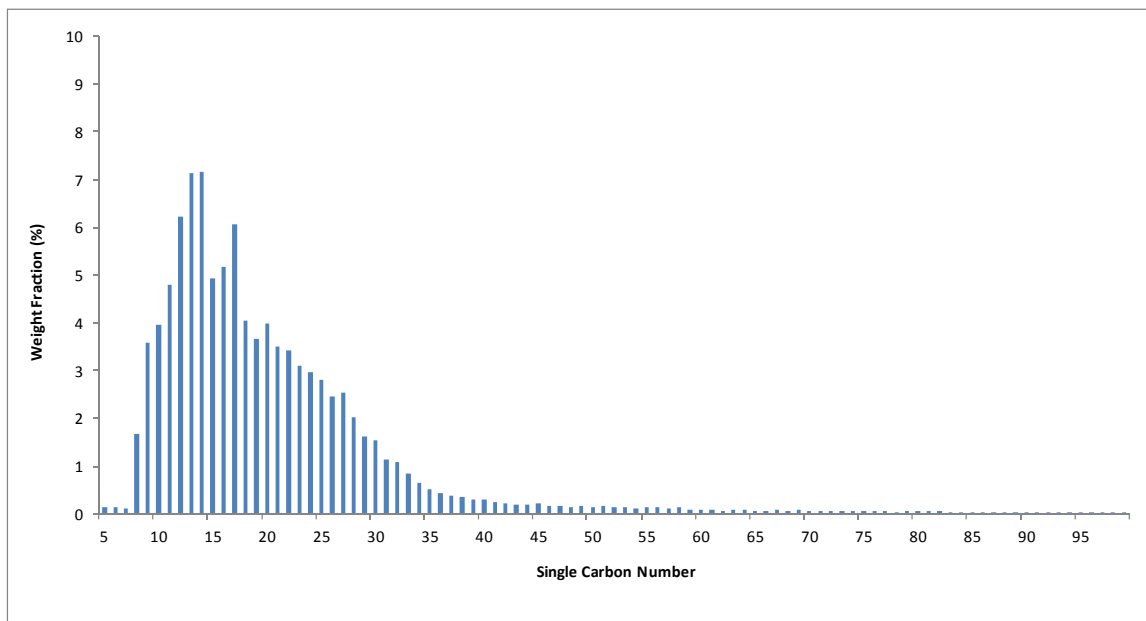
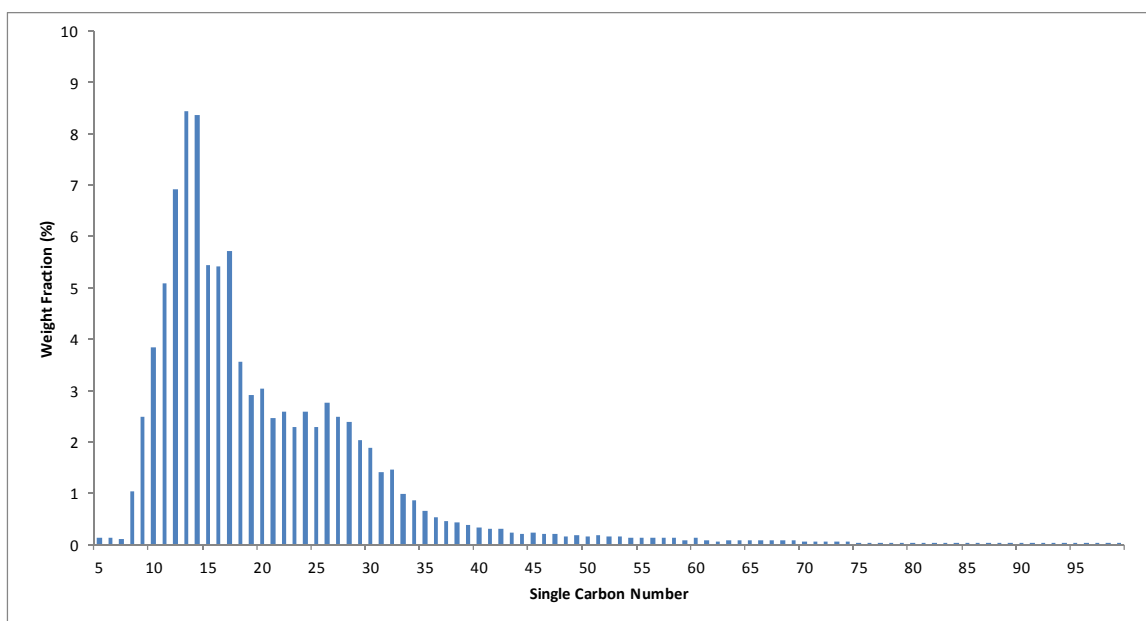
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APPENDIX A: SARA FRACTIONS ANALYSIS FOR OIL A

Table A-1: SARA fractions analysis for the original Oil A and the produced oil from nitrogen injection Test 1 and air injection Tests 2, 3, and 4

Sample	Saturates wt%	Aromatics wt%	Resins wt%	Asphaltenes wt%
Original Oil A	70.9	19.4	9.7	0.8
Produced Oil				
Test 1	76.2	16.6	7.2	0.6
Test 2	66.6	14.8	18.6	0.6
Test 3	71.1	17.7	11.2	0.9
Test 4	73.5	20.1	6.4	0.7

APPENDIX B: SIMULATED DISTILLATION ANALYSIS**Figure B-1: Carbon number distribution of produced oil from N2 injection Test 1****Figure B-2: Carbon number distribution of produced oil from air injection Test 2**

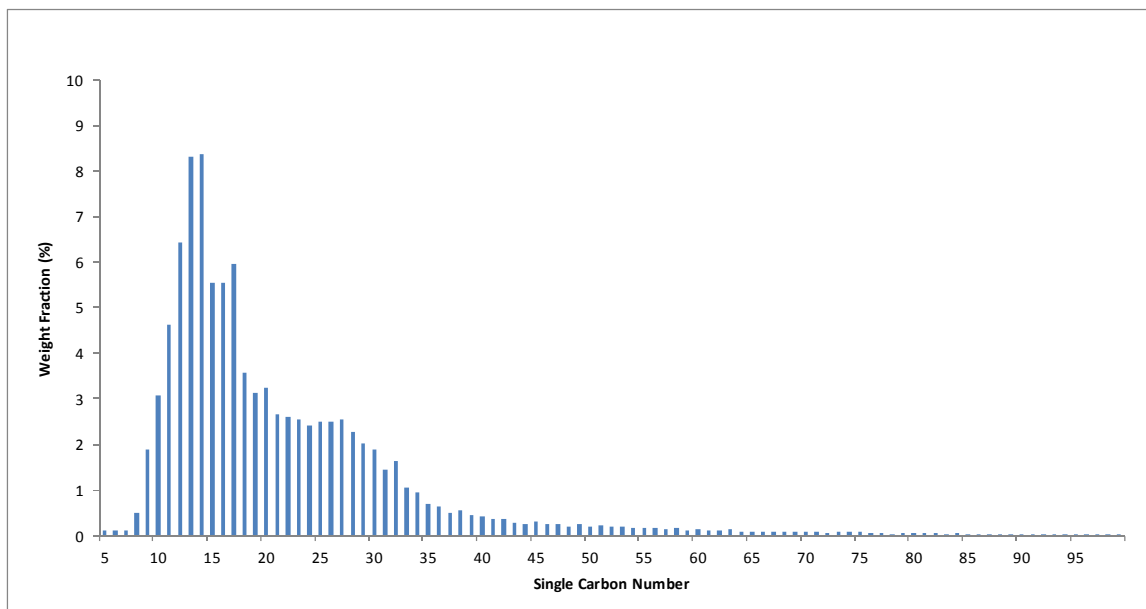


Figure B-3: Carbon number distribution of produced oil from air injection Test 3

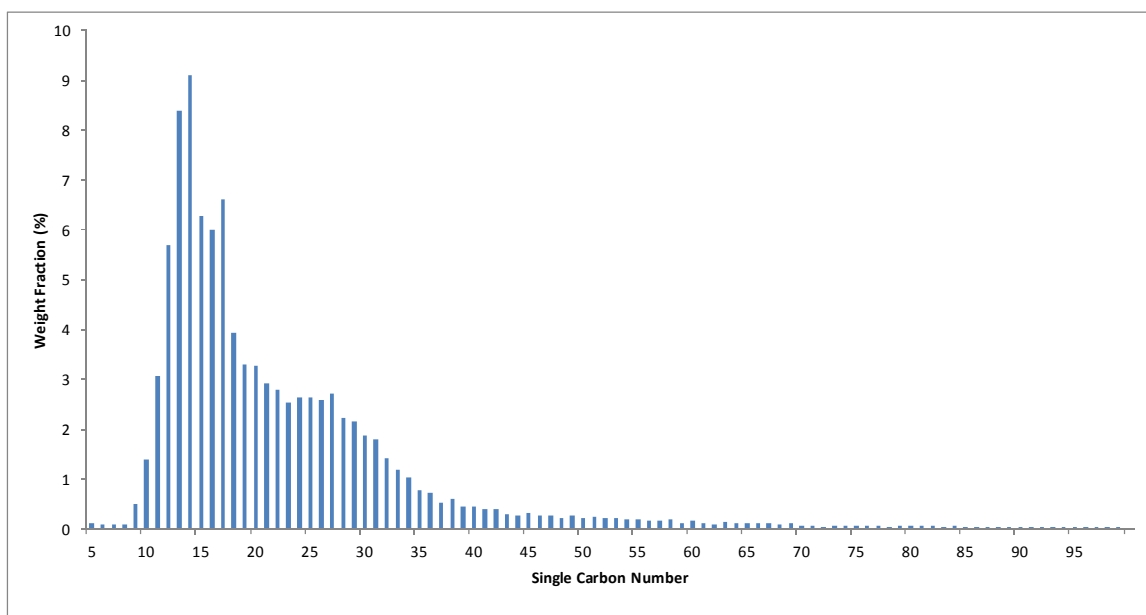


Figure B-4: Carbon number distribution of produced oil from air injection Test 4

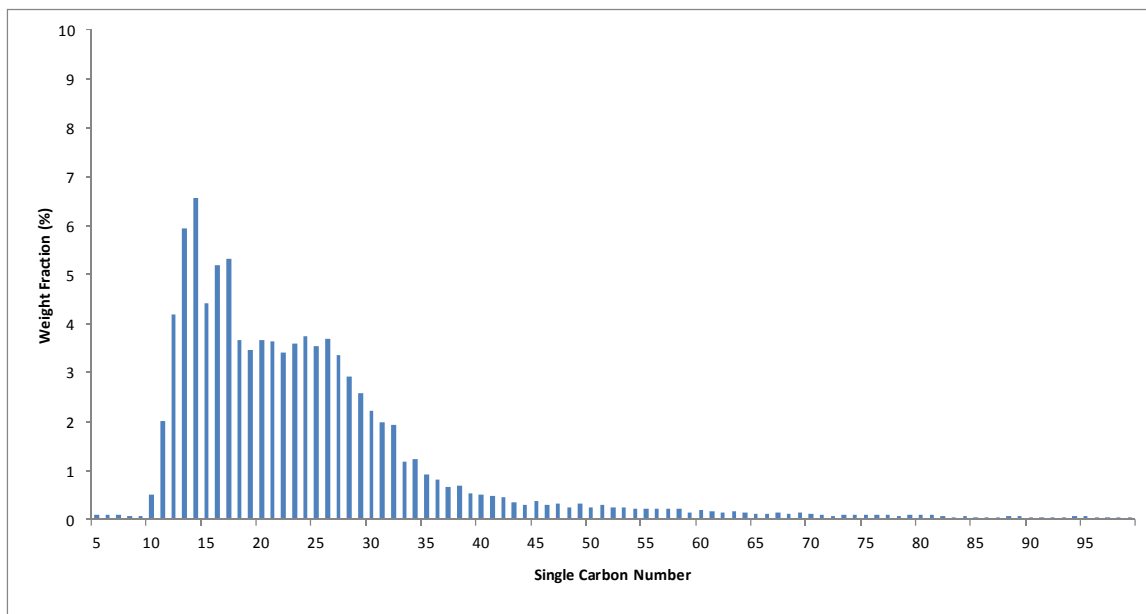


Figure B-5: Carbon number distribution of produced oil from N2 injection Test 5

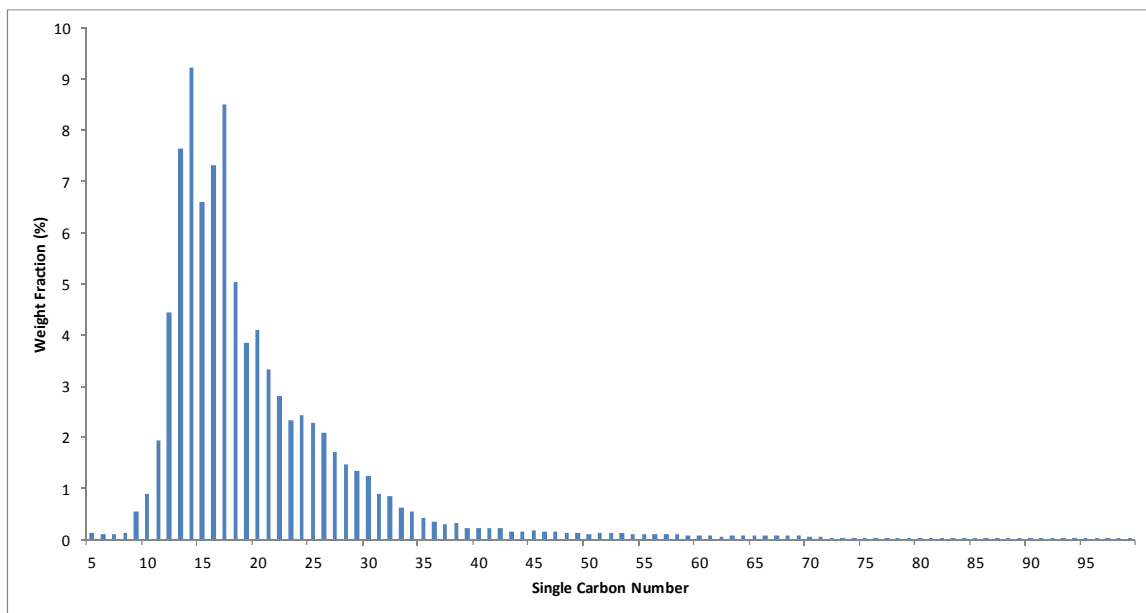


Figure B-6: Carbon number distribution of produced oil from air injection Test 6

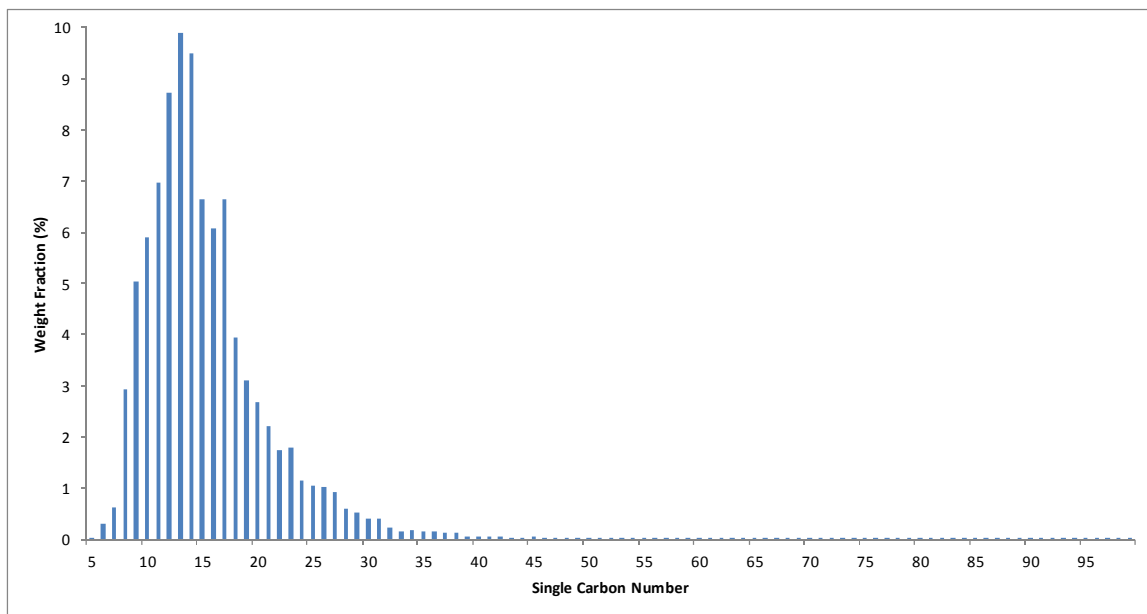


Figure B-7: Carbon number distribution of produced oil from N2 injection Test 7

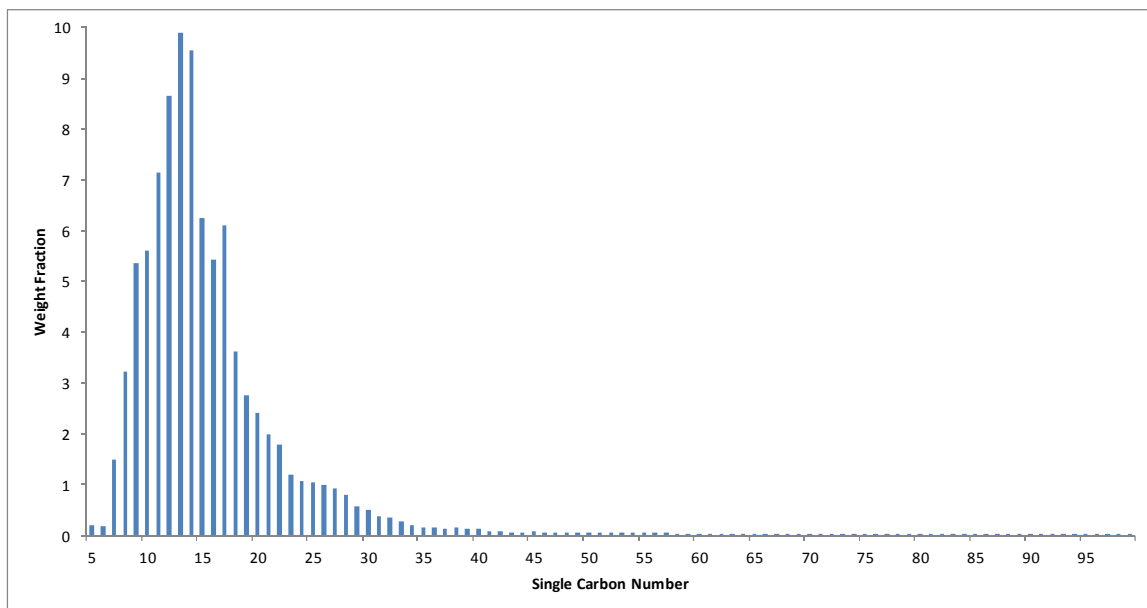


Figure B-8: Carbon number distribution of produced oil from air injection Test 8

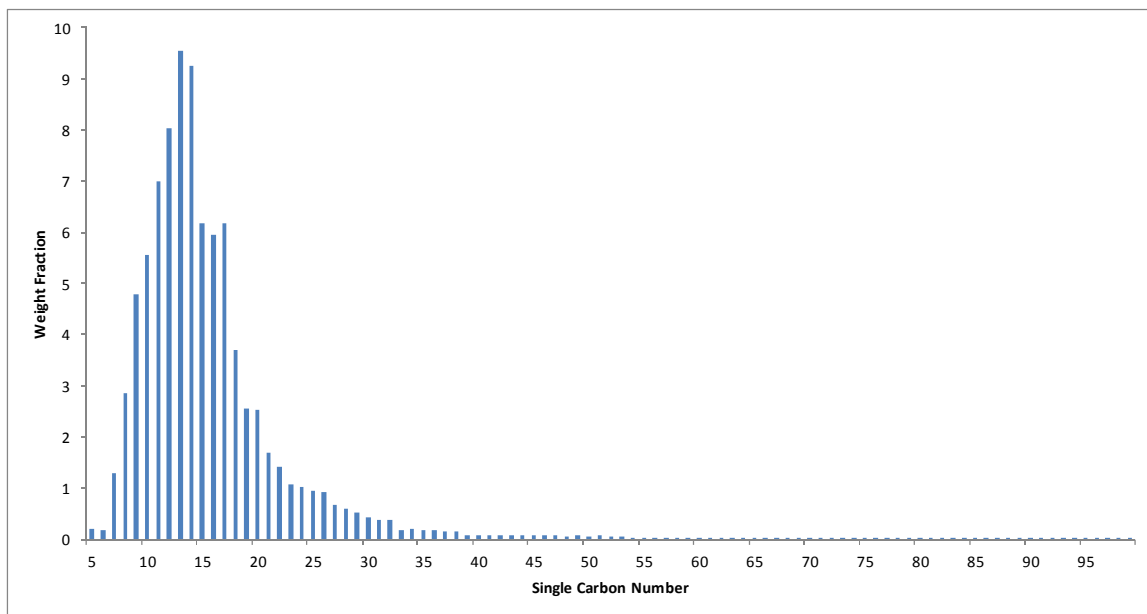


Figure B-9: Carbon number distribution of produced oil from air injection Test 9

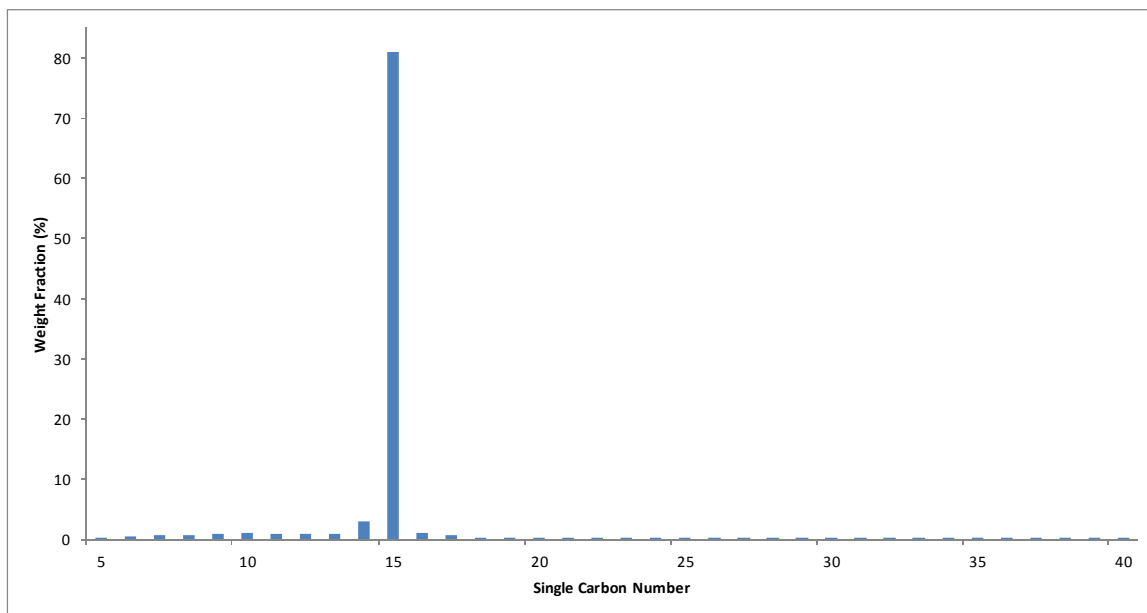


Figure B-10: Carbon number distribution of produced oil from air injection Test 10

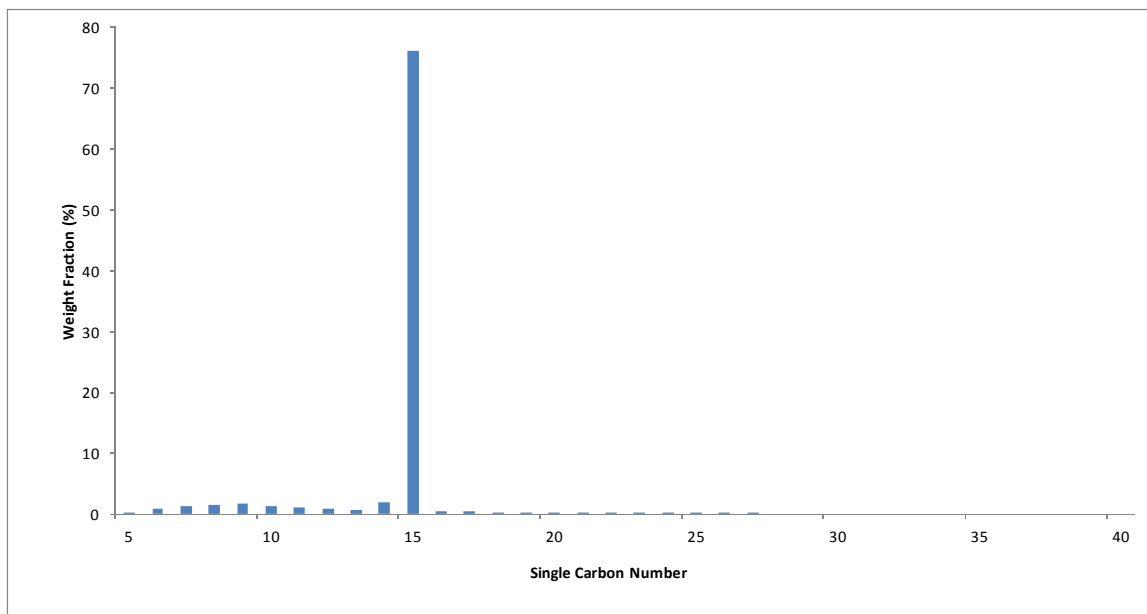


Figure B-11: Carbon number distribution of produced oil from air injection Test 11

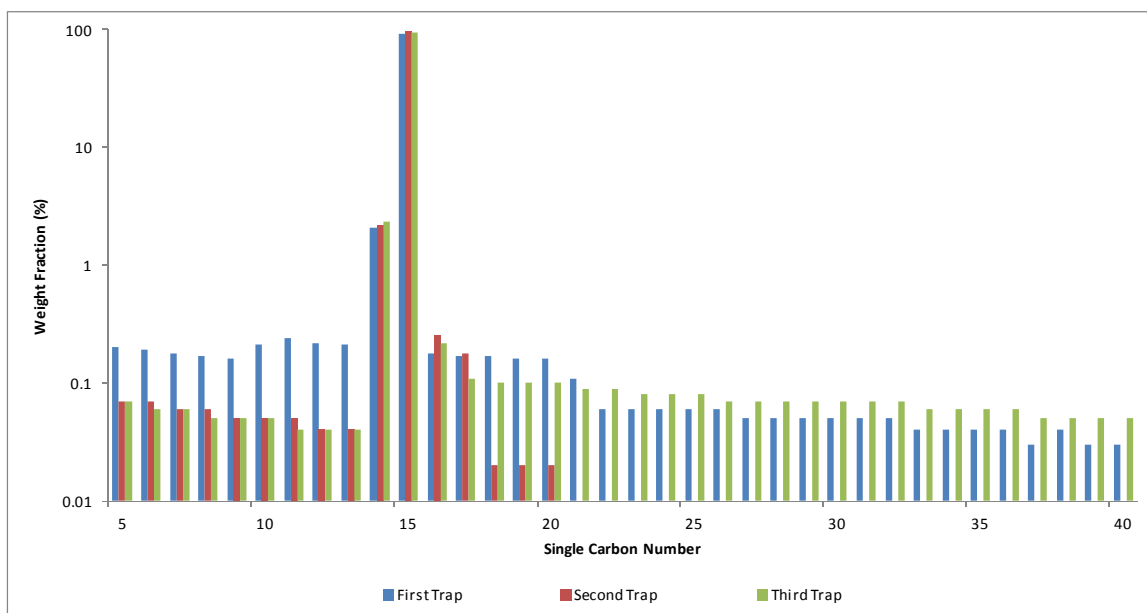


Figure B-12: Carbon number distribution of produced oil from N2 injection Test 12

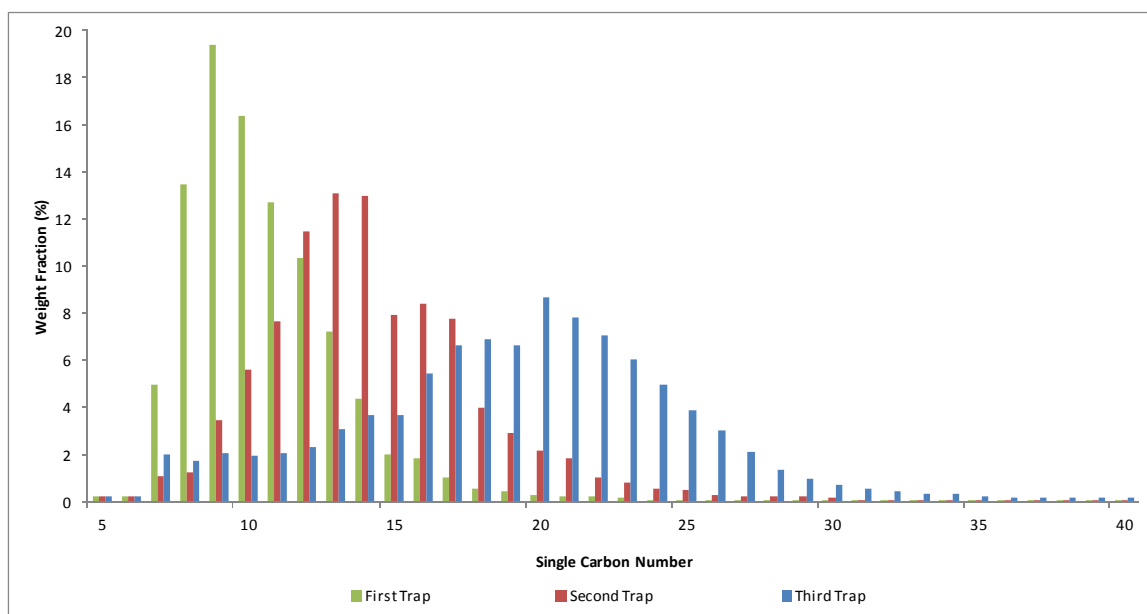


Figure B-13: Carbon number distribution of produced oil from N2 injection Test 13

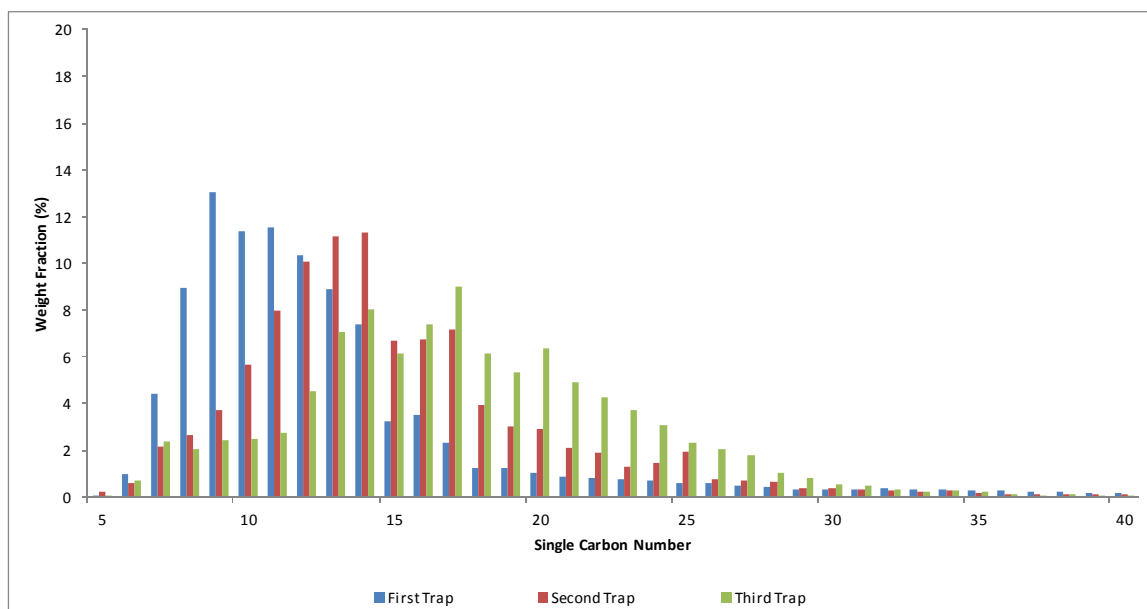
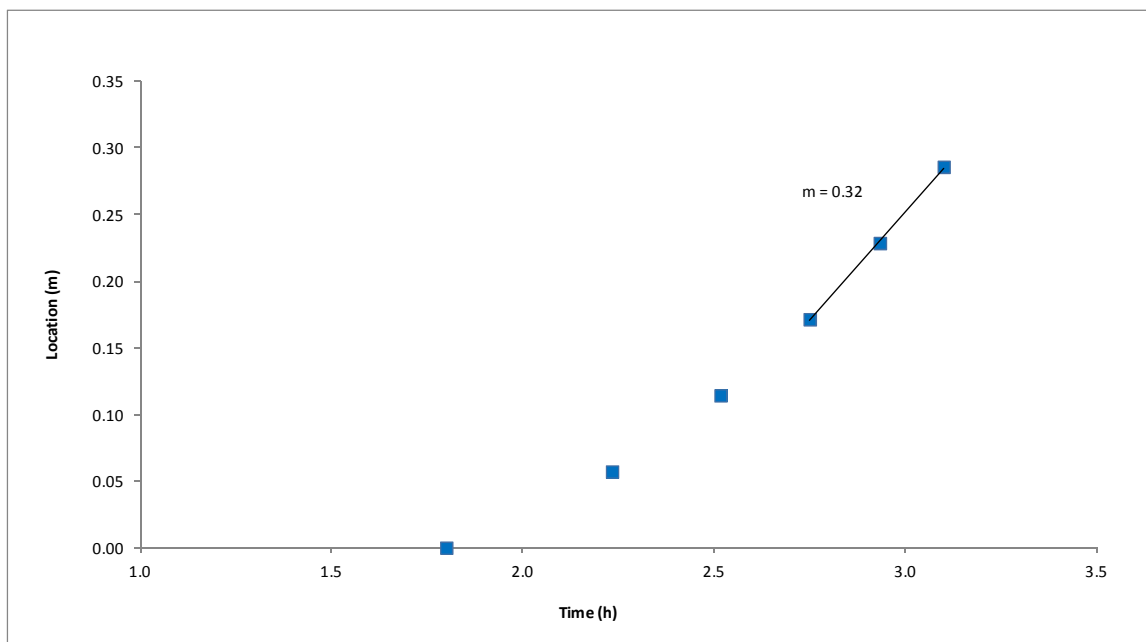
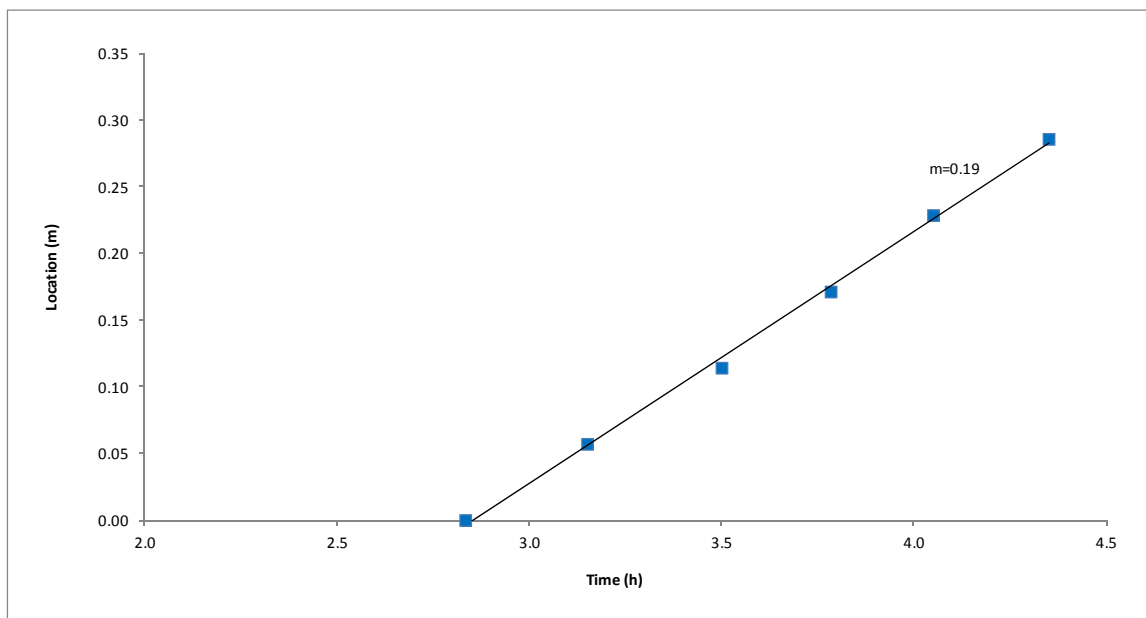


Figure B-14: Carbon number distribution of produced oil from air injection Test 15

APPENDIX C: VELOCITY OF THE EVAPORATION AND COMBUSTION FRONTS**Figure C-1: Evaporation front velocity in Test 1****Figure C-2: Combustion front velocity in Test 2**

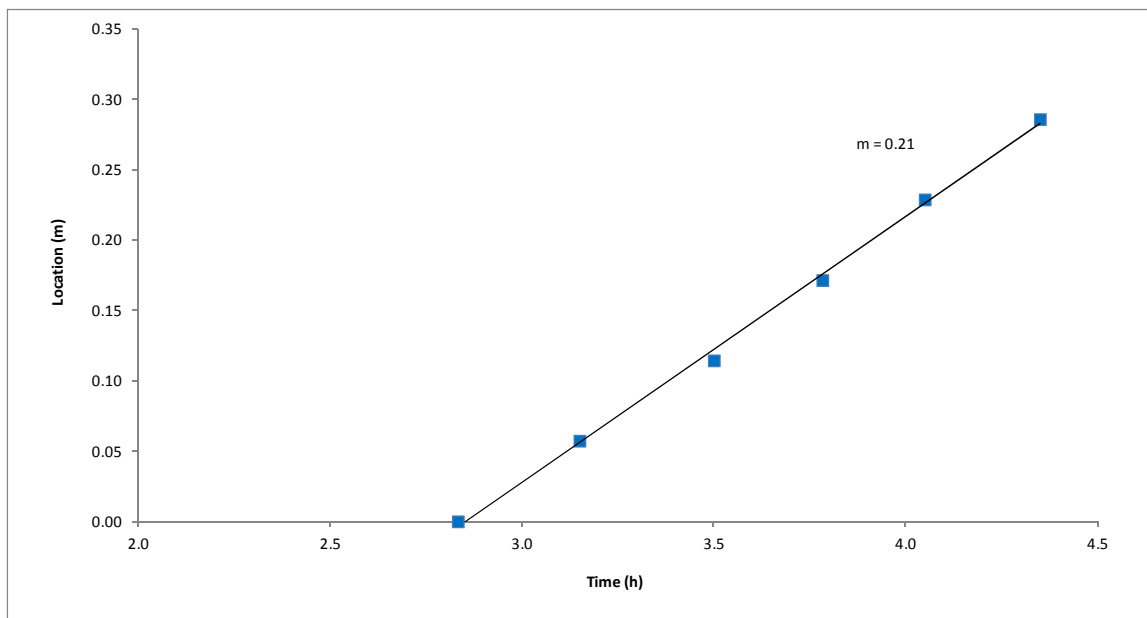


Figure C-3: Combustion front velocity in Test 3

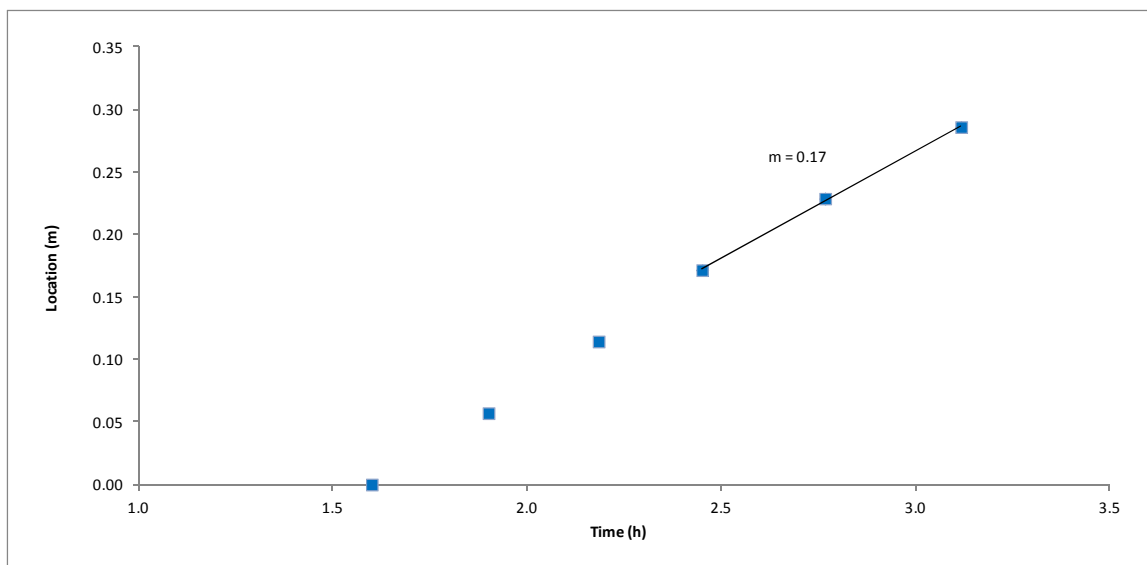


Figure C-4: Combustion front velocity in Test 4

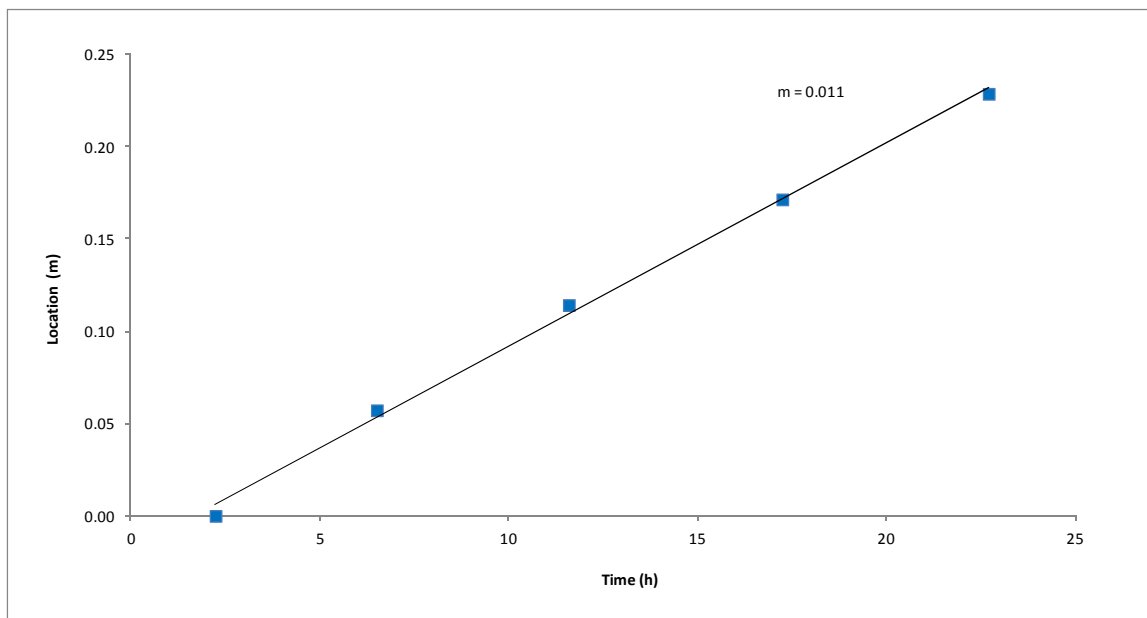


Figure C-5: Evaporation front velocity in Test 5

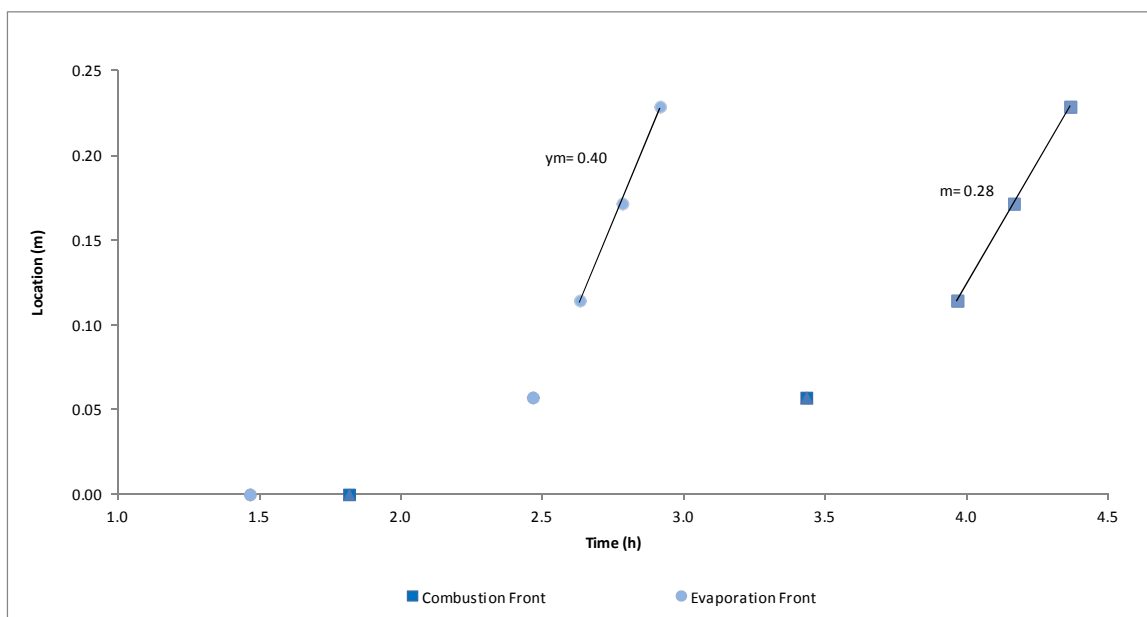


Figure C-6: Combustion and evaporation fronts' velocities in Test 6

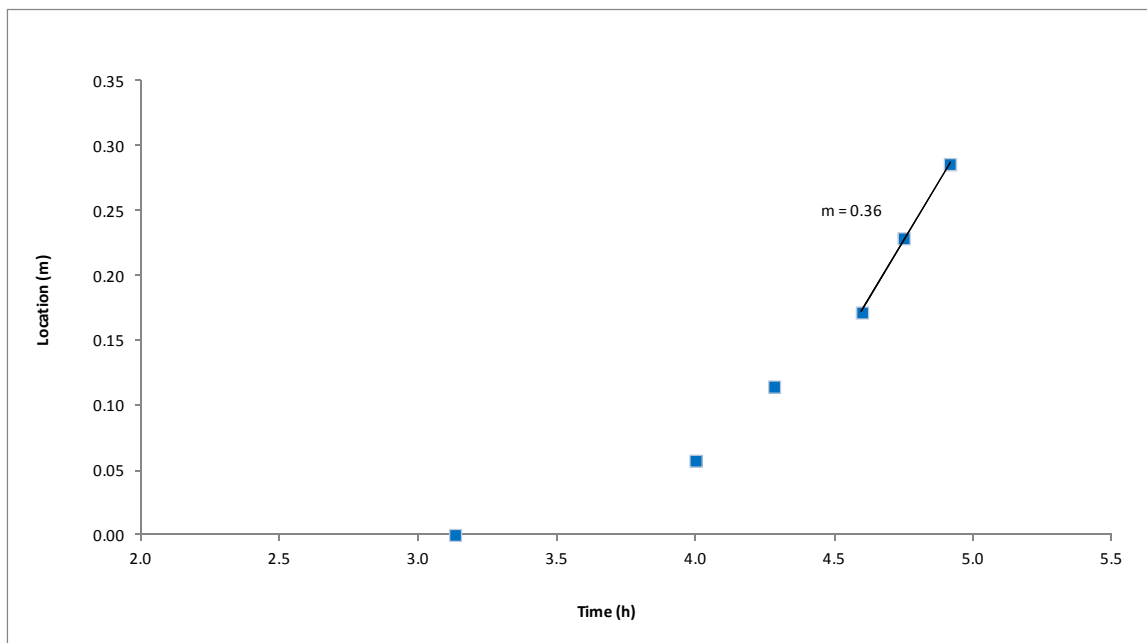


Figure C-7: Evaporation front velocity in Test 7

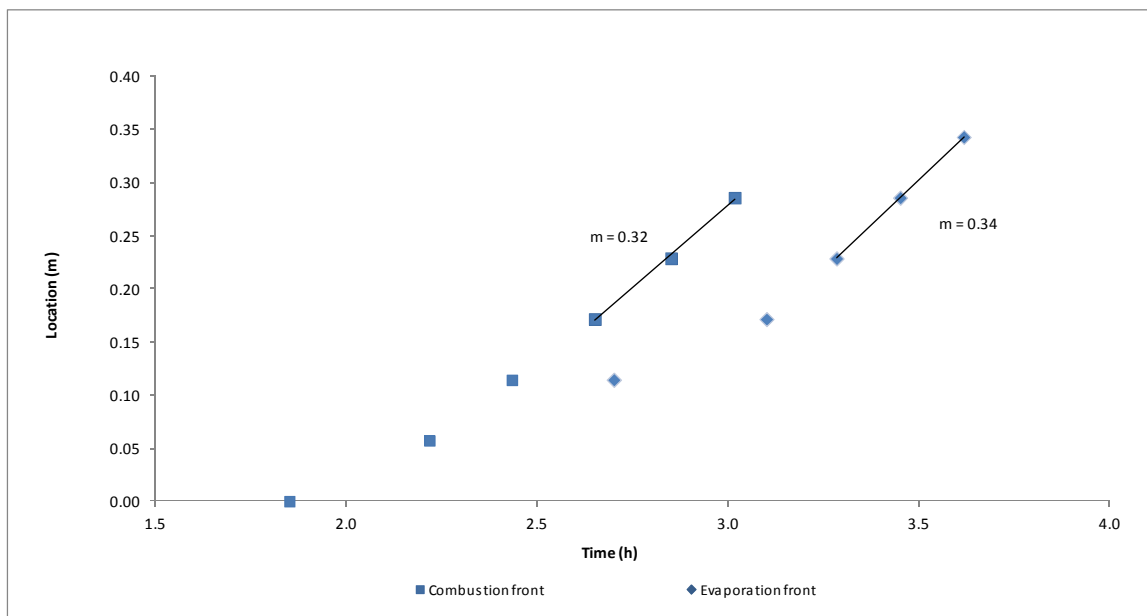


Figure C-8: Combustion and evaporation fronts' velocities in Test 10

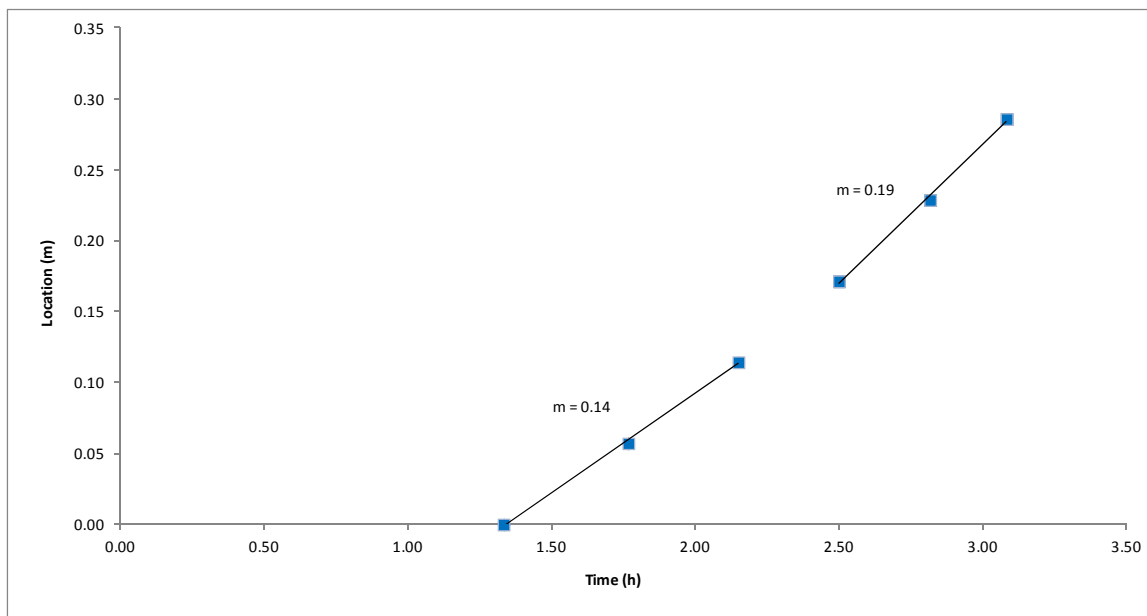


Figure C-9: Combustion front velocity in Test 11

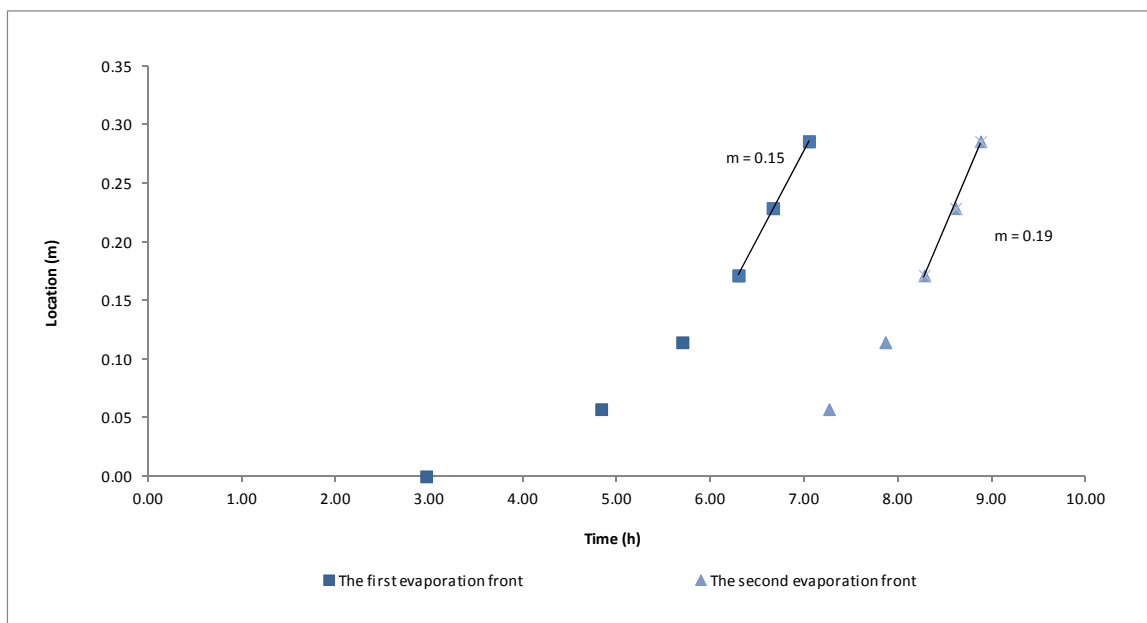


Figure C-10: First and second evaporation fronts' velocities in Test 12

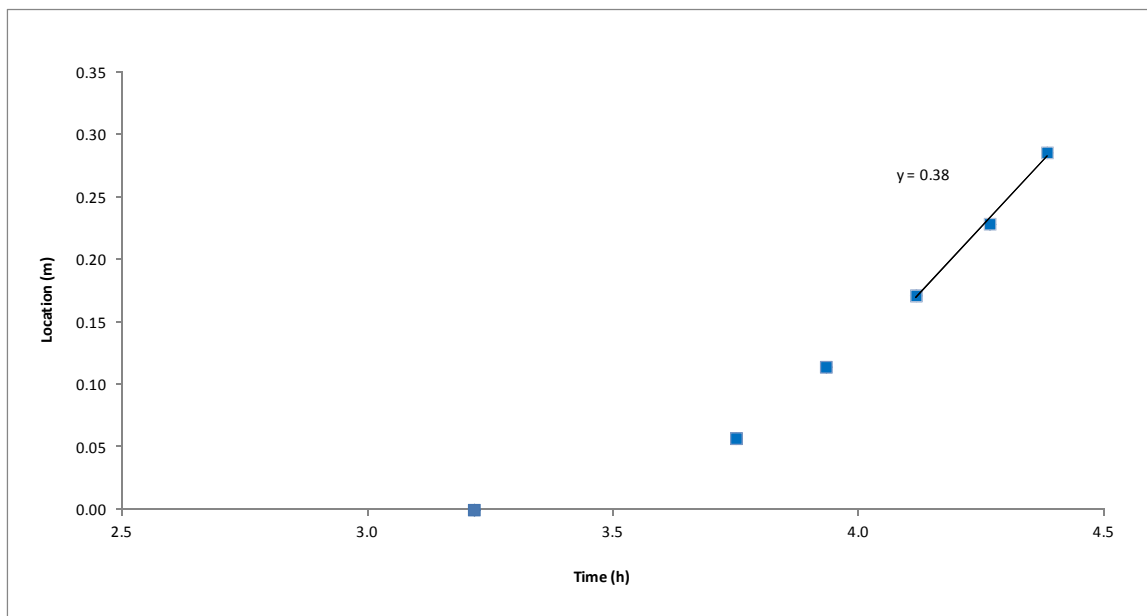


Figure C-11: Evaporation front velocity in Test 14

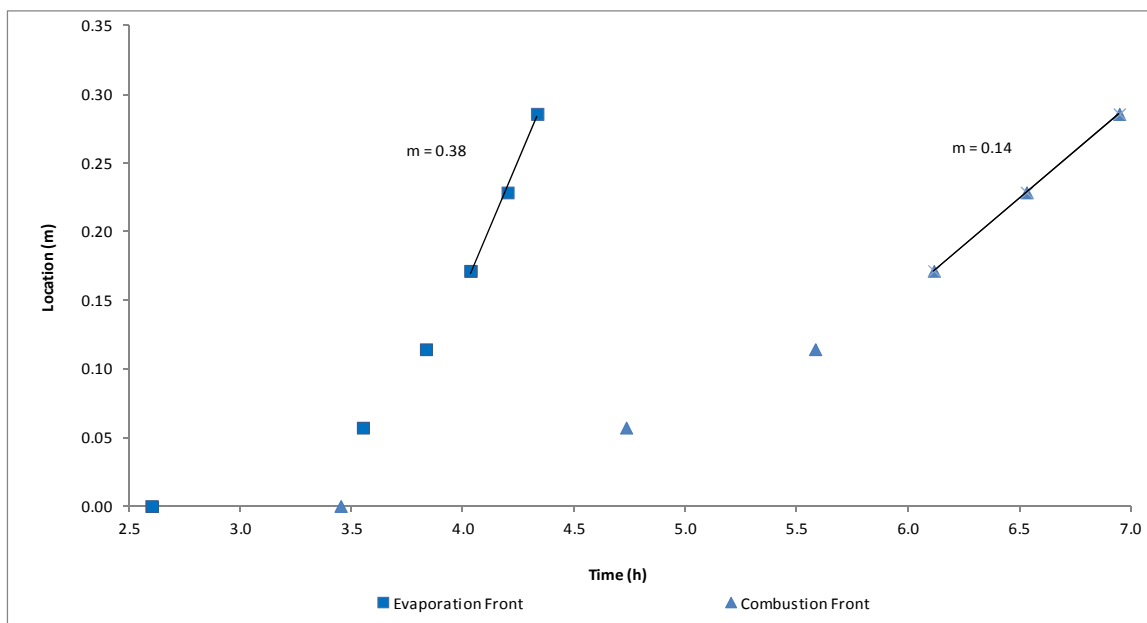


Figure C-12: Combustion and evaporation fronts' velocities in Test 15

Table C-1: Velocity of the visible evaporation and combustion fronts

Test no.	Initial liquids	Injection gas	Flux (sm ³ /m ² h)	Heating ramp (°C/h)	Velocity of combustion (m/h)	Velocity of Evaporation (m/h)
1	Oil A + water	N ₂	38.2	75		0.32
2	Oil A + water	Air	38.2	60	0.19	0.34
3	Oil A + water	Air	38.2	60	0.21	0.34
4	Oil A + water	Air	38.2	40	0.17	
5	Oil A + water	N ₂	38.2	0		0.01
6	Oil A + water	Air	12.7	60	0.30	0.40
7	Oil A + water	N ₂	25.4	60		0.36
10	nC ₁₅ H ₃₂ + water	Air	38.2	60	0.32	0.34
11	nC ₁₅ H ₃₂	Air	38.2	60	0.19	
12	nC ₁₅ H ₃₂ + water	N ₂	38.2	30		0.15(1 st), 0.19(2 nd)
14	water	N ₂	38.2	60		0.38
15	Oil A + water	Air	12.7	60	0.14	0.38

APPENDIX D: GAS PHASE PARAMETERS FOR THE AIR INJECTION TESTS

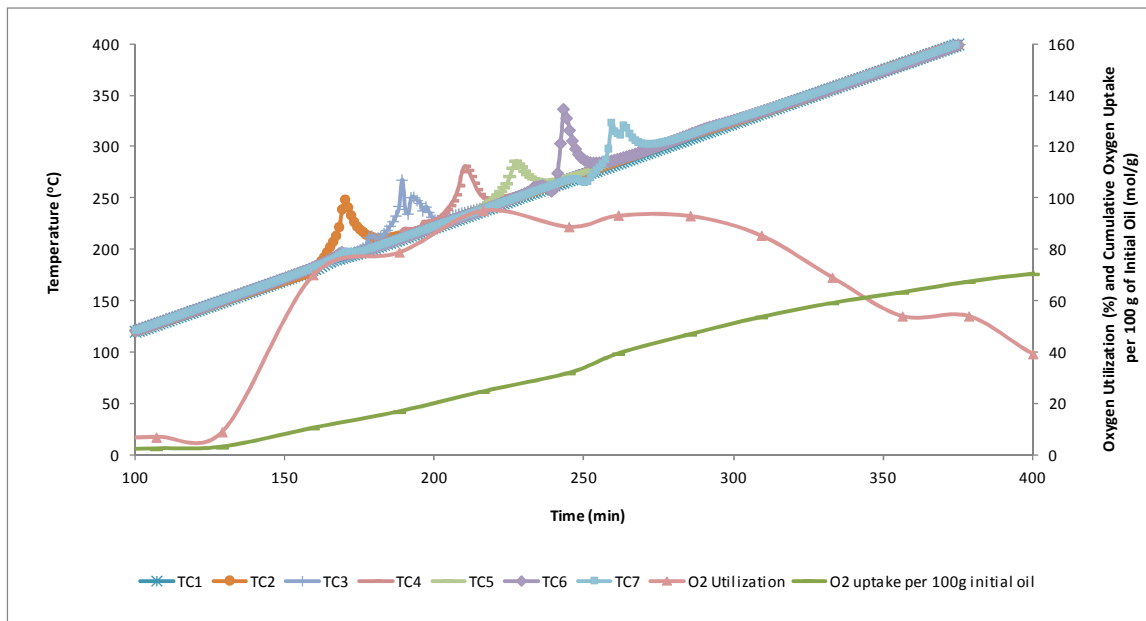


Figure D-1: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 2

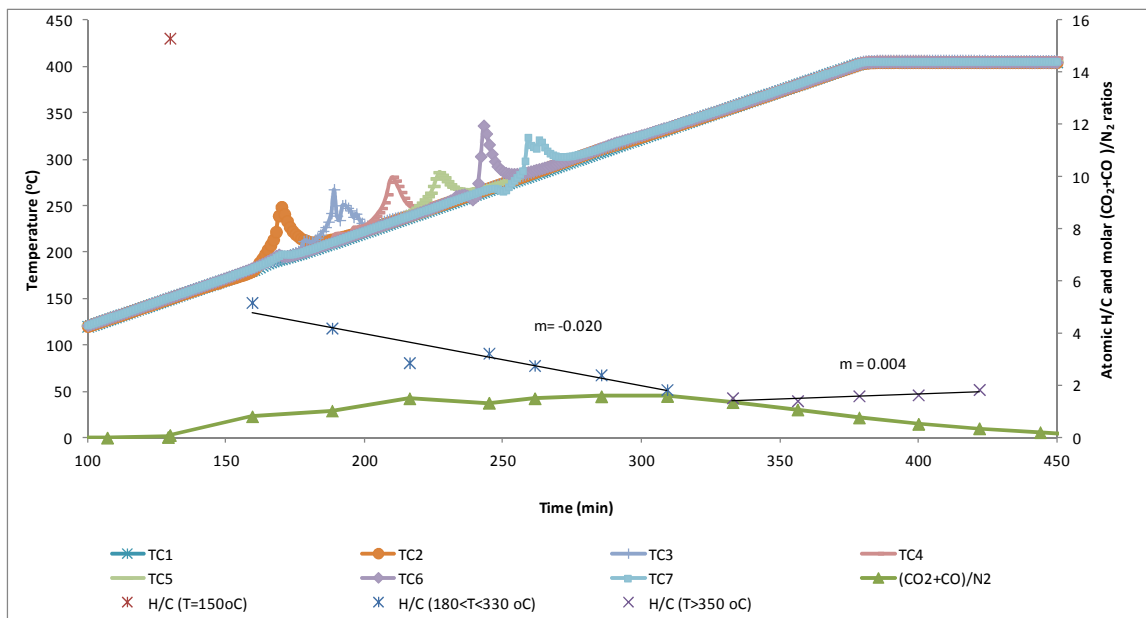


Figure D-2: Apparent atomic H/C ratio and molar carbon oxides to nitrogen ratio with regard to the temperature history as calculated for Test 2

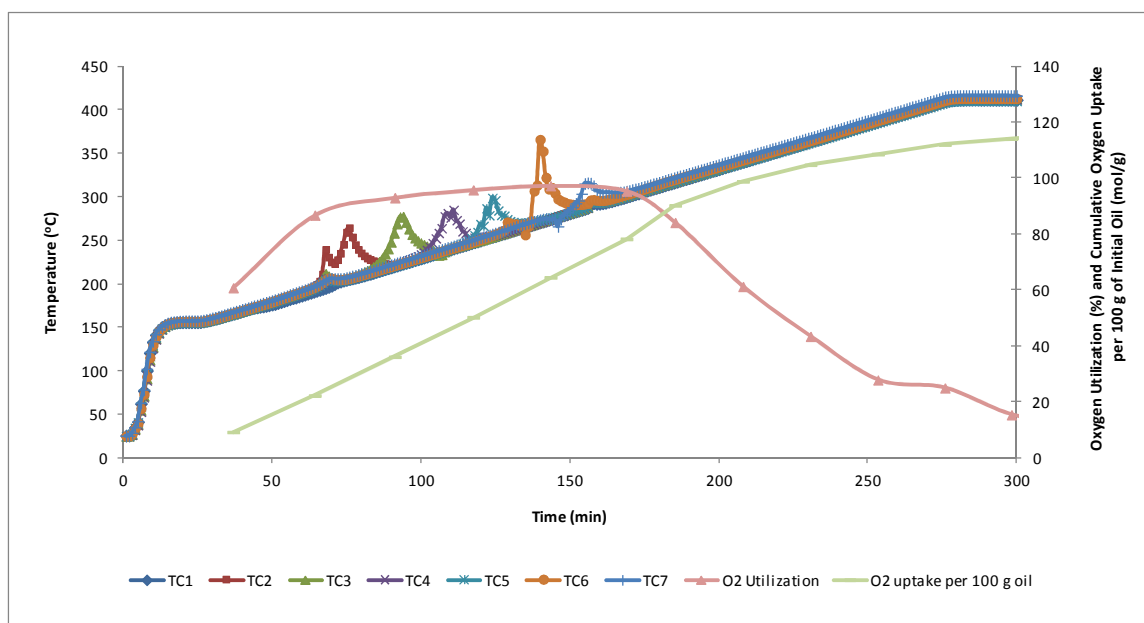


Figure D-3: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 3

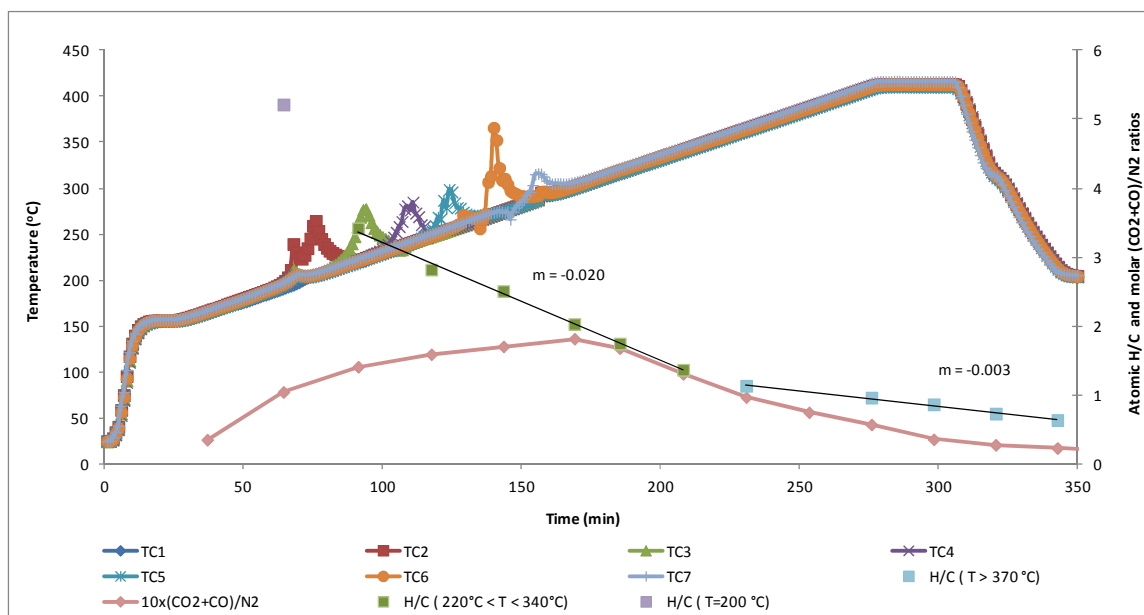


Figure D-4: Apparent atomic H/C ratio and molar carbon oxides to nitrogen ratio with regard to the temperature history as calculated for Test 3

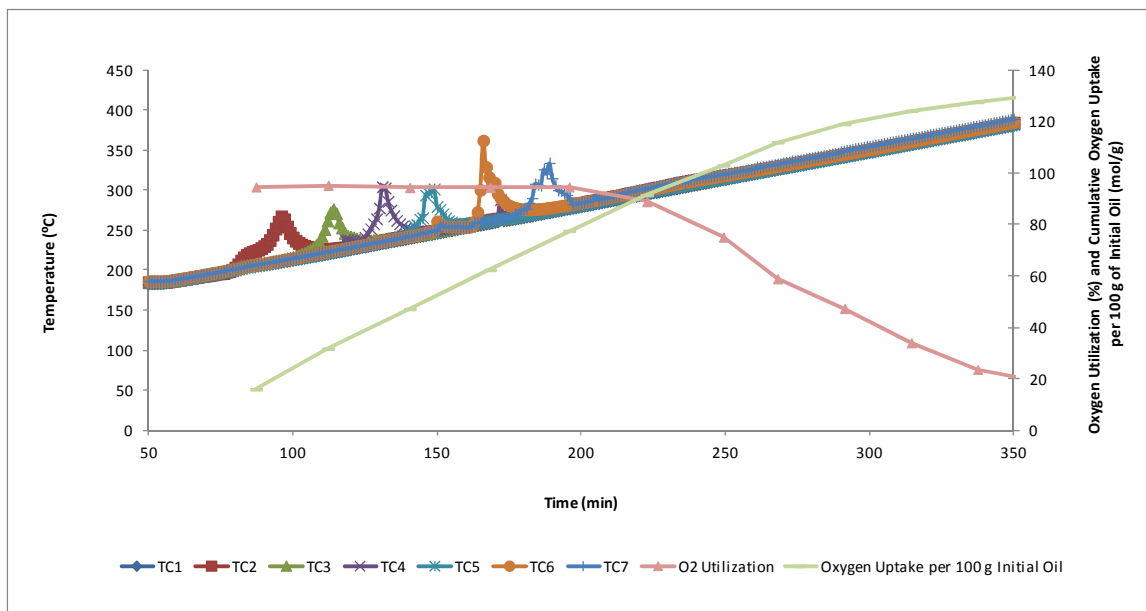


Figure D-5: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 4

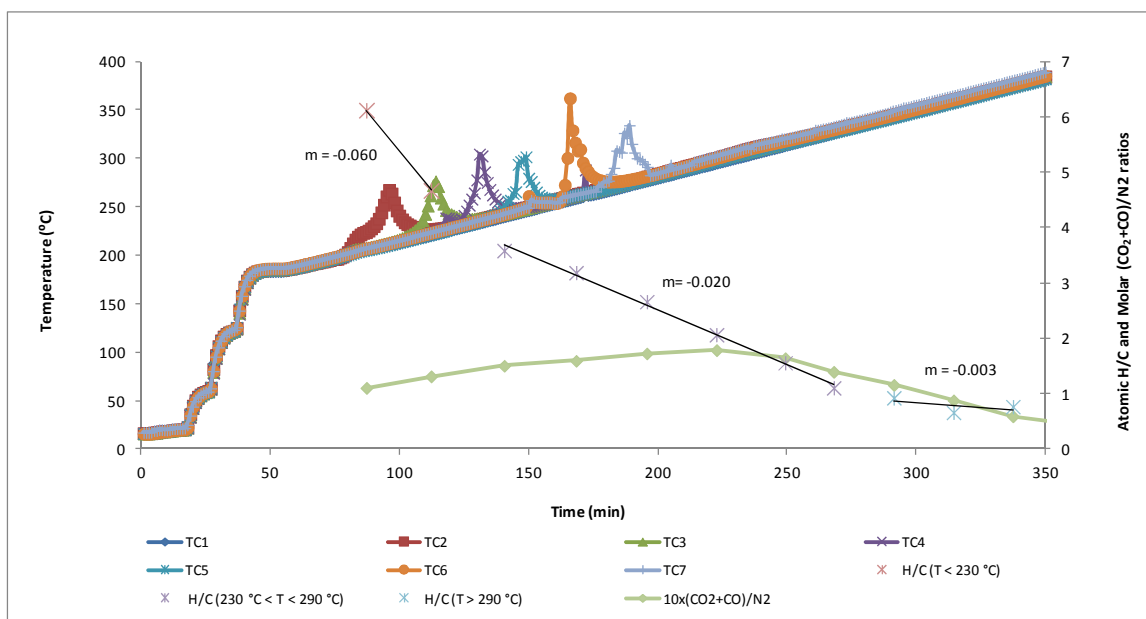


Figure D-6: Apparent atomic H/C ratio and molar carbon oxides to nitrogen ratio with regard to the temperature history as calculated for Test 4

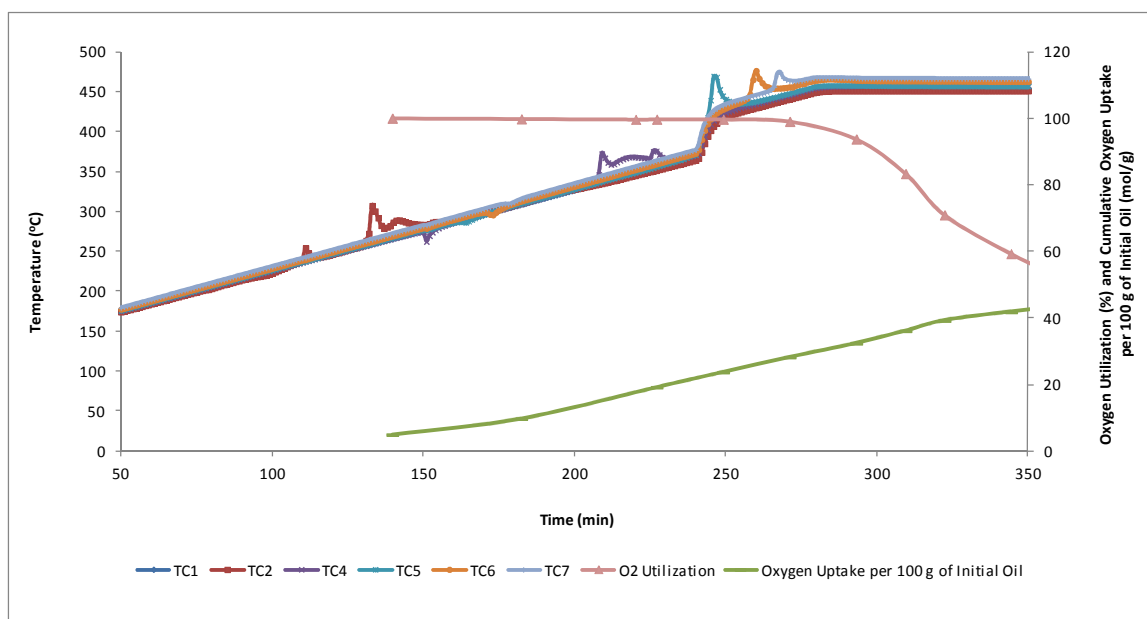


Figure D-7: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 6

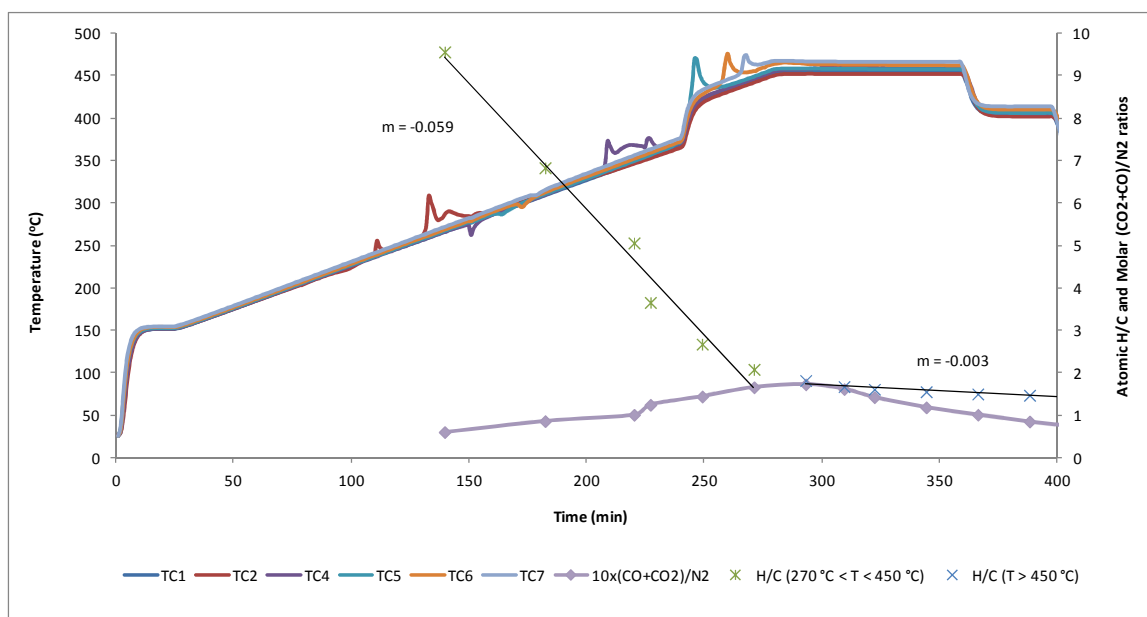


Figure D-8: Apparent atomic H/C ratio and molar carbon oxides to nitrogen ratio with regard to the temperature history as calculated for Test 6

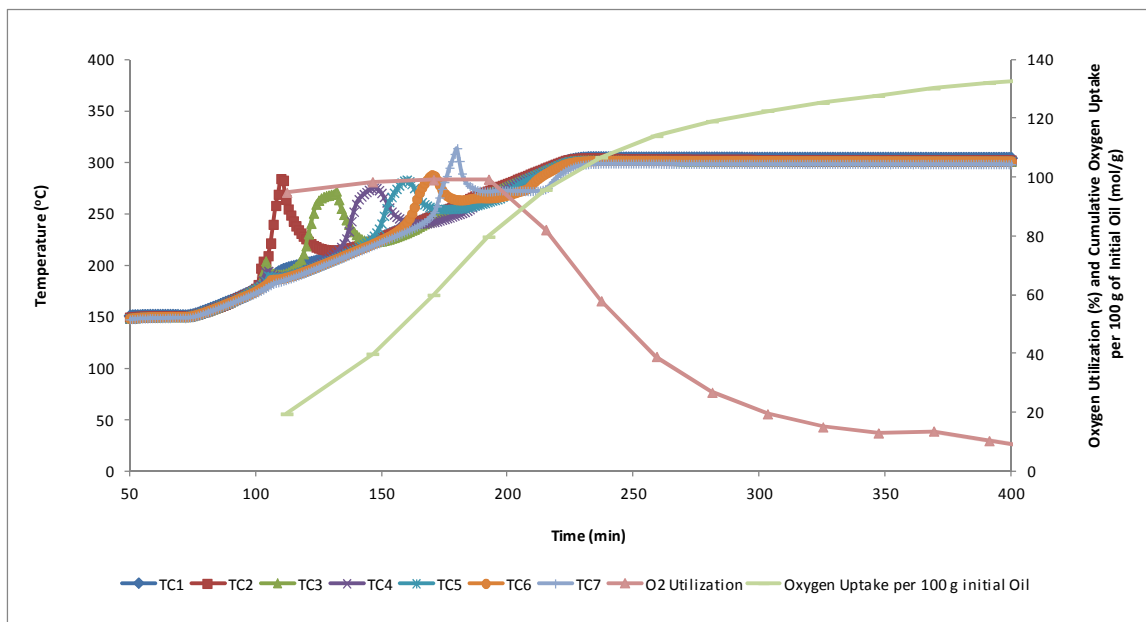


Figure D-9: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 10

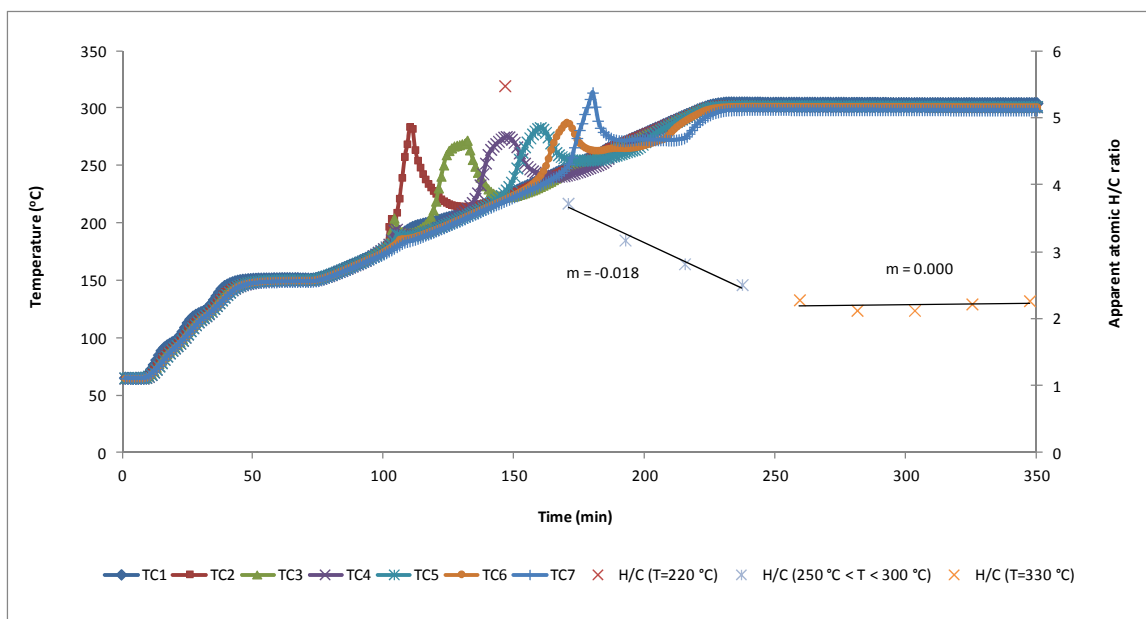


Figure D-10: Apparent atomic H/C ratio with regard to the temperature history as calculated for Test 10

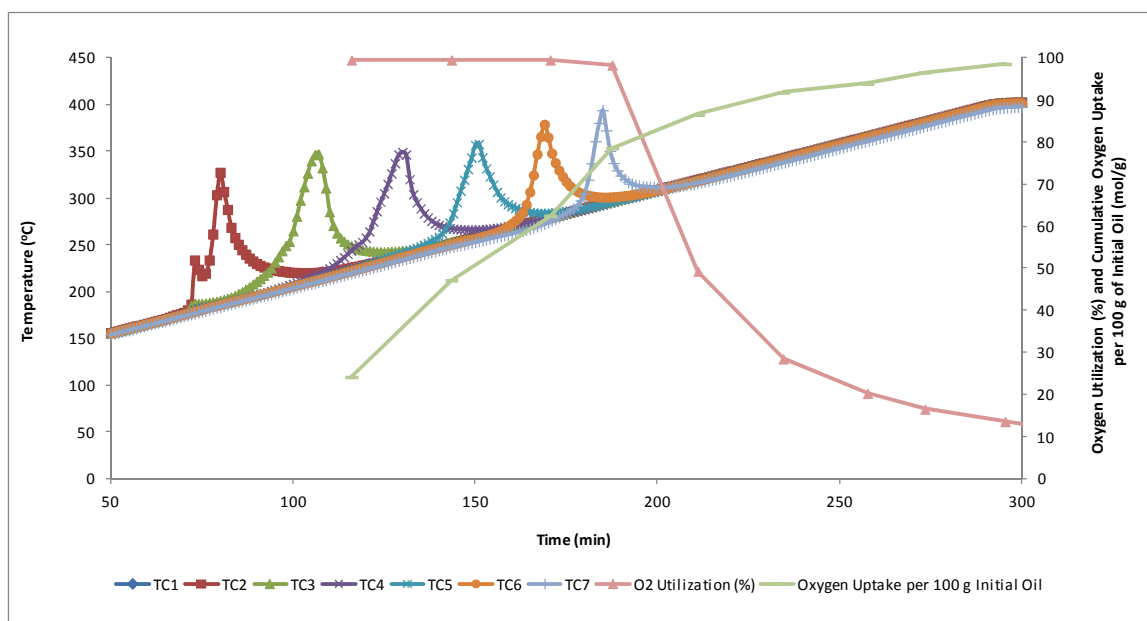


Figure D-11: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 11

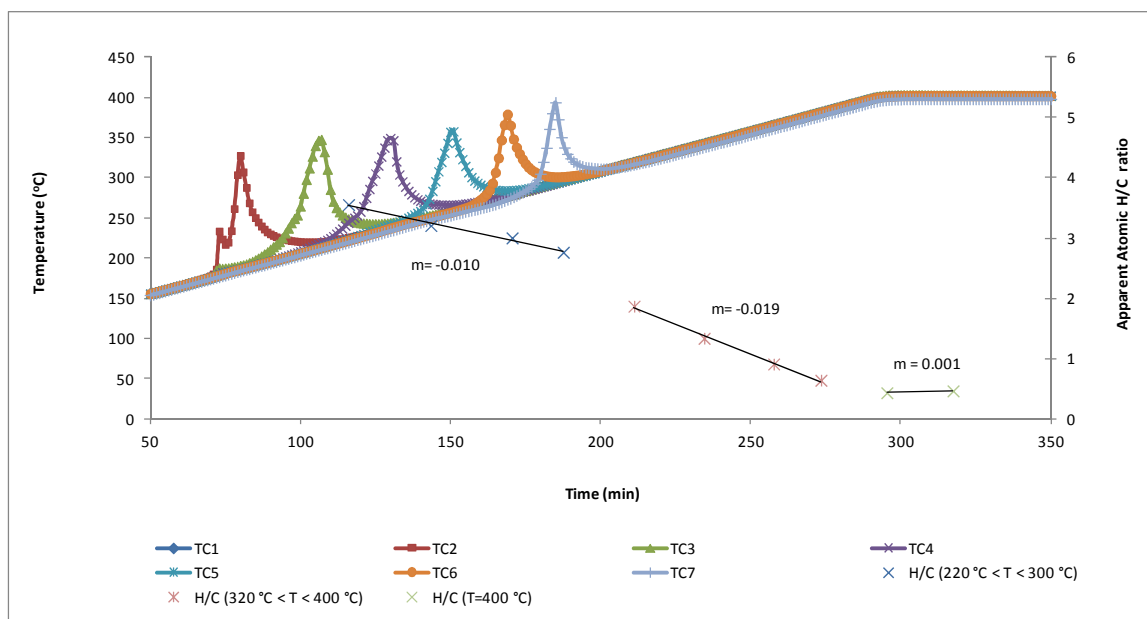


Figure D-12: Apparent atomic H/C ratio with regard to the temperature history as calculated for Test 11

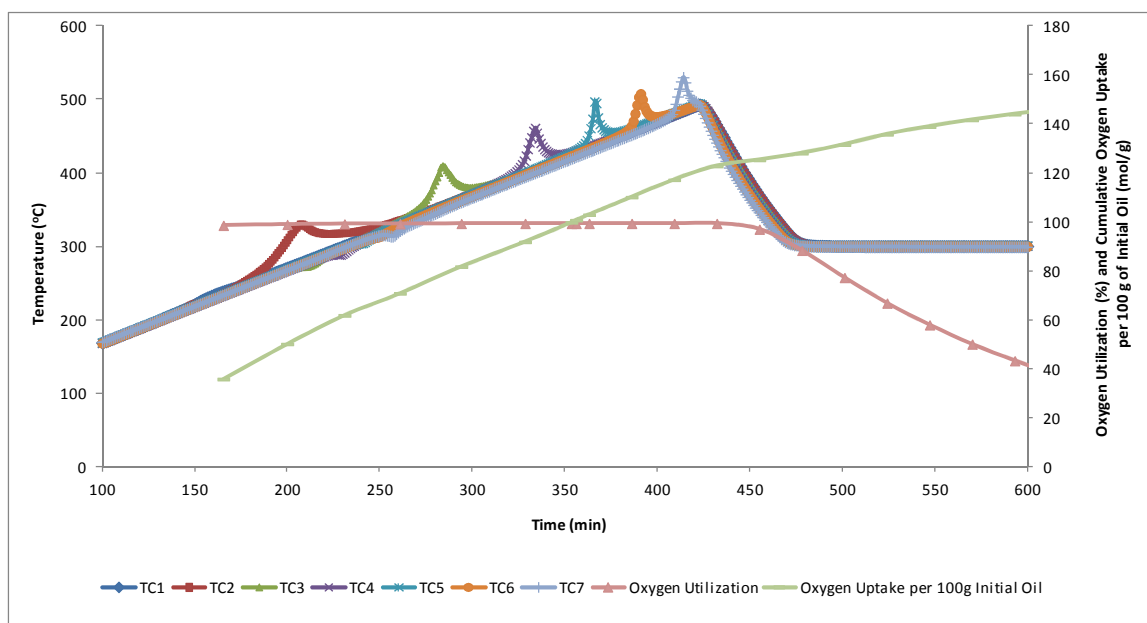


Figure D-13: Oxygen utilization and oxygen uptake per 100g of initial oil with regard to the temperature history as calculated for Test 15

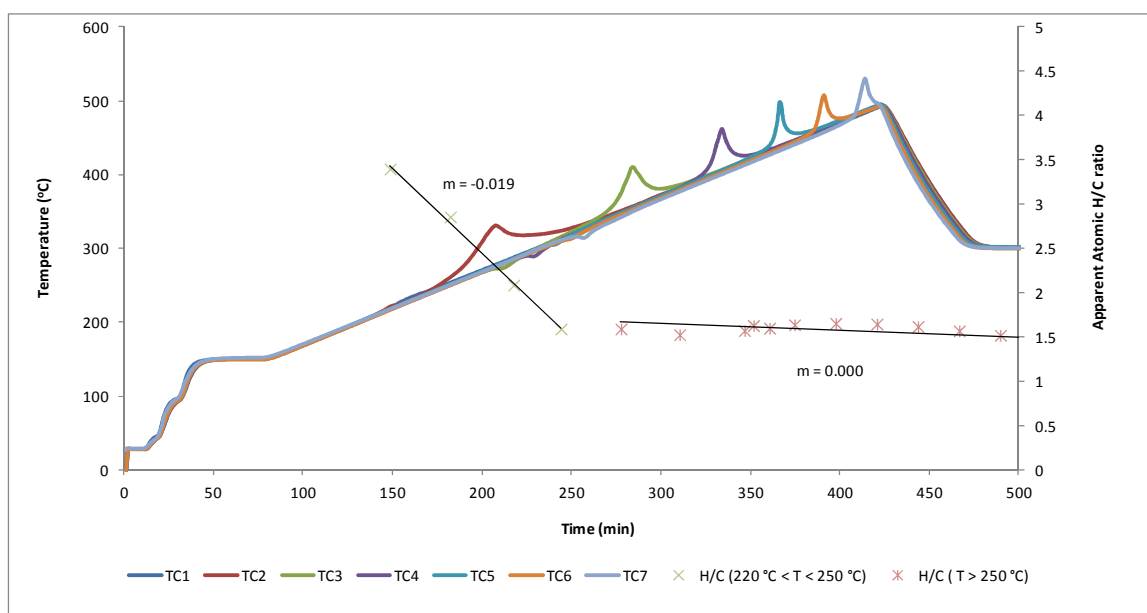


Figure D-14: Apparent atomic H/C ratio with regard to the temperature history as calculated for Test 15